Air Emission Reduction from the Use of Alternative Fuels in Cement Production

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Abstract

The brisk increase in recent global industrialisation and development has sourced similar demands for the provision of construction materials. Cement being a fundamental ingredient used, and the global rate of cement production is predicted to reach 6.1 billion tonnes in 2050. Cement manufacturing is a resource and energy intensive industry which utilises 9% of global industrial energy and is accountable for 5 per cent of carbon dioxide (CO$_2$) emissions. Given the endothermic reactions required to produce 1 tonne of cement, it also consequently releases 1 tonne of CO$_2$ into the atmosphere, propagating that future emissions from manufacturing are also set to double. With its effects towards climatic impacts receiving recent wide-spread attention, the agenda of avoiding CO$_2$ emissions still requires immediate regulatory support and action to control a rising and irreversible baseline.

Further to climatic effects, concerned health effects from pollutant exposure can include particulate matter (PM), oxides of nitrogen (NO$_x$) and sulfur oxides (SO$_x$). If manufacturing is not well engineered or emissions are not fully abated, various other air pollutants can also be released, including heavy metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-\(p\) dioxins and furans (PCDD/F) and polychlorinated biphenyls (PCB). Through research and experimental examination, the cement manufacturing process is identified with a great potential to reduce these pollutants and energy needs through the substitution of combustible waste fuels which contain sufficiently energy, namely alternative derived fuels (ADF).

As the physical and chemical structure of ADFs may differ within and between material types, the formation, suspension, control and release of contaminants will largely dependent on a combination of fuel composition, process design and operation, and combustion conditions. The challenge, however, is that a change or increased influence on one or more of these attributes is shown to affect process stability (with upsets), heat loss or corrosion, increased emissions or a reduced production capacity (due to build-ups or blockages). Discovering process bottlenecks will pave the way for optimising waste co-incineration within cement manufacturing. This thesis investigated ADF co-incineration in several cement plants under normal conditions, and to identify factors which influence the formation of criteria air pollutants. The objective is to provide process data and changes to a pollutant’s unit mass emission factor (UMEF) can be minimal when
compared to baseline emissions, and that the complete destruction and irreversible transformation of pollutants is achieved. The thesis also examines any impacts to the rate of clinker production and if any bottlenecks formed.

In summary, the co-incineration trials of waste oil, carbon dust, waste solvents and shredded tyres within differing cement kilns were shown to have the minimal influence on baseline emission rates, or had significantly reduced pollutants’ UMEF. Specific to the waste oil trials, the reported levels were significantly lower than the baseline averages for total solid particulate (TSP), CO₂, acid gases, volatile organic compounds (TVOCs), sulfur oxides (SOₓ), heavy metals, and polychlorinated biphenyls (PCBs). For the carbon dust trials, the results achieved less than the baseline averages for carbon monoxide (CO), PCDD/F, and PCBs. The co-incineration of waste chemical solvents resulted in lower emission levels than baseline averages for TSP, CO, TVOCs, heavy metals, polycyclic aromatic hydrocarbons (PAH), PCDD/F, and PCBs. For the burning of tyres, sample results showed to be less than baseline emissions TSP, CO₂, SOₓ, PAH, PCDD/F, and PCBs. Furthermore, an increased rate of substituted fuel during the experimental also identified a consistent reduction to health-critical emissions of particulates, heavy metals, dioxins and dl-PCBs. The distribution of toxic isomers (TCDD/F and PeCDD/F) were shown to be predominate during waste oil, wood chips, and solvent trials. Whereas the use of TDFs consistently showed a lower toxicity contribution. The distribution of dl-PCBs toxic congeners showed PCB-126 (3,3’,4,4’,5-Pentachloro biphenyl) to be greatly present during the co-incineration of waste oil, wood chips, solvents and TDF trials.

For each test burn, the rotary kiln presented the typical requirements for hazardous waste incineration, particularly high combustion temperatures, extended fuel-flame residence time, gas turbulence, stoichiometric mixing, thermal inertia, existing post-combustion pollutant techniques and no waste residual for further disposal. Of particular interest to this thesis is that even with the co-incineration of an increasing ADF%, monitoring has identified there to be no subsequent emission effects and that the key process parameters contributing to contaminant suppression included (1) precalciner and kiln fuel firing rate and residence time; (2) preheater and precalciner gas and material temperature; (3) rotary kiln flame temperature and residence time; (4) fuel-air ratio and percentage of excess oxygen; and (5) the mass flow of meal feed and clinker load.

This thesis has shown the above various techniques and inputs are viable for suppressing the formation of air pollutants whilst providing the necessary combustion and calcination
needs, and that regulatory agencies should encourage the technological innovations needed to meet air quality goals along with the co-incineration of alternative waste fuels.
Statement of Originality

This work has not previously been submitted for a degree or diploma in any university. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is made in the thesis itself.

Glen Richards
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Nomenclature

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<thead>
<tr>
<th>Term / Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>Thermal diffusivity.</td>
</tr>
<tr>
<td>ρ</td>
<td>Fluid density.</td>
</tr>
<tr>
<td>%I</td>
<td>Percent isokinetic.</td>
</tr>
<tr>
<td>ΔP</td>
<td>Pressure drop.</td>
</tr>
<tr>
<td>λₚ</td>
<td>Fuel particle thermal conductivity.</td>
</tr>
<tr>
<td>µg</td>
<td>Micrograms (10⁻⁶ grams).</td>
</tr>
<tr>
<td>µg/Nm³</td>
<td>Micrograms per normalised cubic meter.</td>
</tr>
<tr>
<td>µg/Sm³</td>
<td>Micrograms per normalised cubic meter, referenced to O₂ or CO₂.</td>
</tr>
<tr>
<td>µg/tonne</td>
<td>Micrograms per tonne.</td>
</tr>
<tr>
<td>µm</td>
<td>Micrometres (10⁻⁶ meters).</td>
</tr>
<tr>
<td>ACS</td>
<td>American Cancer Society.</td>
</tr>
<tr>
<td>ADF</td>
<td>Alternative derived fuel (also referenced as low-carbon fuel).</td>
</tr>
<tr>
<td>ADF%</td>
<td>Substitution percentage of alternative derived fuel (by weight).</td>
</tr>
<tr>
<td>ADF₇</td>
<td>Alternative derived fuel feed rate.</td>
</tr>
<tr>
<td>Air</td>
<td>Rate of air intake.</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Aluminium oxide.</td>
</tr>
<tr>
<td>APCD</td>
<td>Air Pollution Control Device.</td>
</tr>
<tr>
<td>As</td>
<td>Arsenic.</td>
</tr>
<tr>
<td>Ba</td>
<td>Barium.</td>
</tr>
<tr>
<td>BaP</td>
<td>Benzo(a)pyrene.</td>
</tr>
<tr>
<td>BaPₑₓ</td>
<td>Total of BaP-TEQ PAH congeners, excluding LOD values.</td>
</tr>
<tr>
<td>BaPᵢⁿ</td>
<td>Total of BaP-TEQ PAH congeners, including LOD values.</td>
</tr>
<tr>
<td>BAT</td>
<td>Best Available Techniques.</td>
</tr>
<tr>
<td>BATRef</td>
<td>BAT reference document for cement production (EU).</td>
</tr>
<tr>
<td>Be</td>
<td>Beryllium.</td>
</tr>
<tr>
<td>Bi</td>
<td>Biot number.</td>
</tr>
<tr>
<td>BMP</td>
<td>Best Management Practises.</td>
</tr>
<tr>
<td>BTX</td>
<td>Benzene, Toluene, Xylene.</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>C\text{C}_{\text{fuel}}</td>
<td>Carbon content.</td>
</tr>
<tr>
<td>CaCO\text{3}</td>
<td>Calcium carbonate.</td>
</tr>
<tr>
<td>CaO</td>
<td>Calcium oxide.</td>
</tr>
<tr>
<td>CaSO\text{4}</td>
<td>Calcium sulphite.</td>
</tr>
<tr>
<td>CC</td>
<td>Carbon content of fuel.</td>
</tr>
<tr>
<td>Cd</td>
<td>Cadmium.</td>
</tr>
<tr>
<td>Cembureau</td>
<td>European Cement Association.</td>
</tr>
<tr>
<td>CH\text{4}</td>
<td>Methane.</td>
</tr>
<tr>
<td>CIAB</td>
<td>Coal Industry Advisory Board (International).</td>
</tr>
<tr>
<td>CIPEC</td>
<td>Canadian Industry Program for Energy Conservation.</td>
</tr>
<tr>
<td>Cl\text{2}</td>
<td>Chlorine.</td>
</tr>
<tr>
<td>CKD</td>
<td>Cement kiln dust.</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon monoxide.</td>
</tr>
<tr>
<td>CO\text{2}</td>
<td>Carbon dioxide.</td>
</tr>
<tr>
<td>CO\text{2}_{\text{e}}</td>
<td>Carbon dioxide equivalent.</td>
</tr>
<tr>
<td>CO\text{2}_{\text{EF}}</td>
<td>Total CO\text{2} emissions from cement manufacturing (calculated).</td>
</tr>
<tr>
<td>CO\text{2}_{\text{SE}}</td>
<td>Specific emission for CO\text{2} per tonne clinker produced (calculated).</td>
</tr>
<tr>
<td>Cr\text{3}\text{+}</td>
<td>Trivalent chromium.</td>
</tr>
<tr>
<td>Cr\text{6}\text{+}</td>
<td>Hexavalent chromium.</td>
</tr>
<tr>
<td>CSI</td>
<td>Cement Sustainability Initiative (subsidiary of WBCSD).</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper.</td>
</tr>
<tr>
<td>CV</td>
<td>Calorific value.</td>
</tr>
<tr>
<td>d\text{p}</td>
<td>Particle aerodynamic diameter.</td>
</tr>
<tr>
<td>D\text{y}</td>
<td>Days operating per year.</td>
</tr>
<tr>
<td>DCC</td>
<td>Department of Climate Change (Australia).</td>
</tr>
<tr>
<td>Dioxins</td>
<td>Term or abbreviation for polychlorinated dibenzo –p dioxins and polychlorinated dibenzo –p furans (see also PCDD/F).</td>
</tr>
<tr>
<td>dl-PCBs</td>
<td>Dioxin-like PCBs.</td>
</tr>
<tr>
<td>DRE</td>
<td>Destruction and removal efficiency.</td>
</tr>
<tr>
<td>EA</td>
<td>Environment Agency (United Kingdom).</td>
</tr>
<tr>
<td>EC</td>
<td>European Commission.</td>
</tr>
<tr>
<td>EF</td>
<td>Emission factor (theoretical) for cement manufacturing.</td>
</tr>
<tr>
<td>EF_{ab}</td>
<td>Emission factor from fuel-type used in certain section of plant.</td>
</tr>
<tr>
<td>EF_{cl}</td>
<td>CO\text{2} emission factor for produced clinker.</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>EF&lt;sub&gt;cp&lt;/sub&gt;</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt; emission factor from clinker produced.</td>
</tr>
<tr>
<td>EF&lt;sub&gt;fc&lt;/sub&gt;</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt; emission factor from fuel combustion.</td>
</tr>
<tr>
<td>EIPPCB</td>
<td>European Integrated Pollution Prevention Control Bureau.</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency.</td>
</tr>
<tr>
<td>ESP</td>
<td>Electrostatic precipitator.</td>
</tr>
<tr>
<td>ETS</td>
<td>European Trading Scheme.</td>
</tr>
<tr>
<td>EU</td>
<td>European Union.</td>
</tr>
<tr>
<td>F&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Fluorine.</td>
</tr>
<tr>
<td>F&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Fourier number.</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Iron oxide.</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron.</td>
</tr>
<tr>
<td>Feed</td>
<td>Average meal feed rate (t/hr).</td>
</tr>
<tr>
<td>GCEC</td>
<td>Global Commission on the Economy and Climate (international).</td>
</tr>
<tr>
<td>GFF</td>
<td>Glass fibre filter.</td>
</tr>
<tr>
<td>GHG</td>
<td>Greenhouse gas.</td>
</tr>
<tr>
<td>GJ</td>
<td>Gigajoules (10&lt;sup&gt;9&lt;/sup&gt; joules).</td>
</tr>
<tr>
<td>GJ/tonne</td>
<td>Gigajoules per tonne.</td>
</tr>
<tr>
<td>Gt</td>
<td>Gigatonnes (10&lt;sup&gt;9&lt;/sup&gt; tonnes).</td>
</tr>
<tr>
<td>GWP</td>
<td>Global warming potential</td>
</tr>
<tr>
<td>h</td>
<td>Fuel particle external heat transfer coefficient.</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>Water vapour.</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Hydrogen peroxide.</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Sulfuric acid.</td>
</tr>
<tr>
<td>HCB</td>
<td>Hexachlorobenzene.</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrogen chloride.</td>
</tr>
<tr>
<td>HF</td>
<td>Hydrofluoric acid.</td>
</tr>
<tr>
<td>Hg</td>
<td>Mercury.</td>
</tr>
<tr>
<td>HHV</td>
<td>High heating (calorific) value of fuel.</td>
</tr>
<tr>
<td>HNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Nitric acid.</td>
</tr>
<tr>
<td>HRGC</td>
<td>High resolution gas chromatography.</td>
</tr>
<tr>
<td>HRMS</td>
<td>HRGC with high-resolution electron impact mass spectrometry.</td>
</tr>
<tr>
<td>hr</td>
<td>Hour.</td>
</tr>
<tr>
<td>IARC</td>
<td>International Agency for Research on Cancer.</td>
</tr>
<tr>
<td>IDF</td>
<td>Induced draft fan.</td>
</tr>
</tbody>
</table>
IEA  International Energy Agency.
IIP  Institute for Industrial Productivity (International).
IM  Immersed moisture.
IPA  Isopropanol.
IPCC  Intergovernmental Panel on Climate Change (International).
ISO  International Organisation for Standardisation.
I-TEQ  International toxic equivalent for PCDD/Fs.
Kf  Kiln fuel calorific value.
Kfr  Kiln burner, fuel firing rate.
Kft  Kiln burner flame, temperature.
Kfrt  Kiln burner flame, residence time.
Kgt  Kiln chamber gas temperature.
Kmt  Kiln chamber material temperature.
Krt  Kiln chamber residence time.
K2SO4  Potassium sulfate.
KMnO4  Potassium permanganate.
kPa  Kilo pascal.
LHV  Low heating (calorific) value of fuel.
Load  Average clinker produced (t/hr).
Loadmt  Average clinker material exit temperature (t/hr).
LOD  Limit of detection.
m/s  Meters per second.
MBM  Meat and bone meal.
mg  Milligrams (10⁻³ grams).
mg/m³  Milligrams per cubic meter.
MgCO₃  Magnesium carbonate.
MgO  Magnesium oxide.
MJ  Mega joules (10⁶ joules).
MJ/kg  Mega joules per kilogram.
MJ/tonne  Mega joules per tonne.
Mn  Manganese.
MSW  Municipal solid waste.
Mtoe  Million tonnes of oil equivalent (1 Mtoe = 11.627 TWh).
mtpa  Million tonnes per annum.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>Nitrogen</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>Sodium</td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
<td></td>
</tr>
<tr>
<td>NATA</td>
<td>National Association of Testing Authority (Australia)</td>
<td></td>
</tr>
<tr>
<td>NATO</td>
<td>North Atlantic Treaty Organisation (International)</td>
<td></td>
</tr>
<tr>
<td>NCE</td>
<td>New Climate Economy (subsidiary of GCEC)</td>
<td></td>
</tr>
<tr>
<td>NDIR</td>
<td>Non Dispersive Infrared analyser.</td>
<td></td>
</tr>
<tr>
<td>NESHAPs</td>
<td>National Emission Standards for Hazardous Air Pollutants (USA).</td>
<td></td>
</tr>
<tr>
<td>ng</td>
<td>Nanograms (10⁻⁹ grams).</td>
<td></td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>Sodium sulfate.</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel</td>
<td></td>
</tr>
<tr>
<td>Nm³</td>
<td>Normalised as volume in dry cubic meters at STP.</td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td>Nitric oxide.</td>
<td></td>
</tr>
<tr>
<td>NO₂</td>
<td>Nitrogen dioxide.</td>
<td></td>
</tr>
<tr>
<td>NOₓ</td>
<td>Oxides of nitrogen (NO, NO₂, and HNO₃).</td>
<td></td>
</tr>
<tr>
<td>NOAA</td>
<td>National Oceanic and Atmospheric Administration (USA).</td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>Oxygen</td>
<td></td>
</tr>
<tr>
<td>Oₑ</td>
<td>Excess air.</td>
<td></td>
</tr>
<tr>
<td>OECD</td>
<td>Organisation for Economic Co-operation and Development.</td>
<td></td>
</tr>
<tr>
<td>PAHs</td>
<td>Polycyclic aromatic hydrocarbons.</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>Lead</td>
<td></td>
</tr>
<tr>
<td>PBDD/F</td>
<td>Polychlorinated dibenzo-p dioxins and furans.</td>
<td></td>
</tr>
<tr>
<td>PC</td>
<td>Precalciner.</td>
<td></td>
</tr>
<tr>
<td>PC₇fuel</td>
<td>Precalciner fuel calorific value.</td>
<td></td>
</tr>
<tr>
<td>PC₇f</td>
<td>Precalciner fuel firing rate.</td>
<td></td>
</tr>
<tr>
<td>PC₇gt</td>
<td>Precalciner gas temperature.</td>
<td></td>
</tr>
<tr>
<td>PC₇mt</td>
<td>Precalciner material temperature.</td>
<td></td>
</tr>
<tr>
<td>PC₇rt</td>
<td>Precalciner residence time.</td>
<td></td>
</tr>
<tr>
<td>PCA</td>
<td>Principle component analysis.</td>
<td></td>
</tr>
<tr>
<td>PCB</td>
<td>Polychlorinated biphenyls.</td>
<td></td>
</tr>
<tr>
<td>PCDD</td>
<td>Polychlorinated dibenzo-p dioxins.</td>
<td></td>
</tr>
<tr>
<td>PCDD/F</td>
<td>Abbreviation of PCDD and PCDF.</td>
<td></td>
</tr>
<tr>
<td>PCDD/F ratio</td>
<td>Contribution ratio of total PCDD to total PCDF.</td>
<td></td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>-----------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>PCDD&lt;sub&gt;ex&lt;/sub&gt;</td>
<td>Total of PCDD and PCDF congeners, excluding LOD values.</td>
<td></td>
</tr>
<tr>
<td>PCDD&lt;sub&gt;in&lt;/sub&gt;</td>
<td>Total of PCDD and PCDF congeners, including LOD values.</td>
<td></td>
</tr>
<tr>
<td>PCDD-Nato&lt;sub&gt;ex&lt;/sub&gt;</td>
<td>Total of NATO '95 I-TEQ PCDD and PCDF congeners, excluding LOD values.</td>
<td></td>
</tr>
<tr>
<td>PCDD-Nato&lt;sub&gt;in&lt;/sub&gt;</td>
<td>Total of NATO '95 I-TEQ PCDD and PCDF congeners, including LOD values.</td>
<td></td>
</tr>
<tr>
<td>PCDD-WHO&lt;sub&gt;ex&lt;/sub&gt;</td>
<td>Total of WHO '05 I-TEQ PCDD and PCDF congeners, excluding LOD values.</td>
<td></td>
</tr>
<tr>
<td>PCDD-WHO&lt;sub&gt;in&lt;/sub&gt;</td>
<td>Total of WHO '05 I-TEQ PCDD and PCDF congeners, including LOD values.</td>
<td></td>
</tr>
<tr>
<td>PCDF</td>
<td>Polychlorinated dibenzo –p furans.</td>
<td></td>
</tr>
<tr>
<td>PeCDD/F</td>
<td>Pentachlorinated dibenzo –p doxins and furans.</td>
<td></td>
</tr>
<tr>
<td>PH</td>
<td>Preheater.</td>
<td></td>
</tr>
<tr>
<td>PH/PC</td>
<td>Preheater-Precalciner configuration.</td>
<td></td>
</tr>
<tr>
<td>PH&lt;sub&gt;gt&lt;/sub&gt;</td>
<td>Preheater gas temperature.</td>
<td></td>
</tr>
<tr>
<td>PH&lt;sub&gt;mt&lt;/sub&gt;</td>
<td>Preheater material temperature.</td>
<td></td>
</tr>
<tr>
<td>PH&lt;sub&gt;rt&lt;/sub&gt;</td>
<td>Preheater residence time.</td>
<td></td>
</tr>
<tr>
<td>PIC</td>
<td>Product of incomplete combustion.</td>
<td></td>
</tr>
<tr>
<td>PJ</td>
<td>Peta joule (10&lt;sup&gt;15&lt;/sup&gt; joules).</td>
<td></td>
</tr>
<tr>
<td>PLS</td>
<td>Partial least square.</td>
<td></td>
</tr>
<tr>
<td>PM</td>
<td>Particulate matter.</td>
<td></td>
</tr>
<tr>
<td>PM&lt;sub&gt;2.5&lt;/sub&gt;</td>
<td>Particulate matter with an equivalent aerodynamic diameter of 2.5 micrometres or less (i.e. d&lt;sub&gt;p&lt;/sub&gt; ≤ 2.5 µm).</td>
<td></td>
</tr>
<tr>
<td>PM&lt;sub&gt;10&lt;/sub&gt;</td>
<td>Particulate matter with an equivalent aerodynamic diameter of 10 micrometres or less (i.e. d&lt;sub&gt;p&lt;/sub&gt; ≤ 10 µm).</td>
<td></td>
</tr>
<tr>
<td>POPs</td>
<td>Persistent organic pollutants.</td>
<td></td>
</tr>
<tr>
<td>ppbv</td>
<td>Parts per billion (volume basis).</td>
<td></td>
</tr>
<tr>
<td>ppmv</td>
<td>Parts per million (volume basis).</td>
<td></td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinyl chloride.</td>
<td></td>
</tr>
<tr>
<td>Q / Q&lt;sub&gt;i&lt;/sub&gt;</td>
<td>Heat loss fraction.</td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>Heat transfer rate.</td>
<td></td>
</tr>
<tr>
<td>QFF</td>
<td>Quartz fibred filter.</td>
<td></td>
</tr>
<tr>
<td>R*</td>
<td>Percent recovery of laboratory surrogate.</td>
<td></td>
</tr>
<tr>
<td>R&lt;sup&gt;2&lt;/sup&gt;</td>
<td>Coefficient of multiple determination.</td>
<td></td>
</tr>
</tbody>
</table>

xx
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rs</td>
<td>Percent recovery of field surrogate.</td>
</tr>
<tr>
<td>RDF</td>
<td>Refuse derived fuel.</td>
</tr>
<tr>
<td>s</td>
<td>Second.</td>
</tr>
<tr>
<td>S&lt;sub&gt;1&lt;/sub&gt;</td>
<td>Oxygen-fuel mixture equivalence ratio</td>
</tr>
<tr>
<td>S-type</td>
<td>Stausseheibe type pitot.</td>
</tr>
<tr>
<td>Sb</td>
<td>Antimony.</td>
</tr>
<tr>
<td>SEC</td>
<td>Standard error of prediction.</td>
</tr>
<tr>
<td>Sm&lt;sup&gt;3&lt;/sup&gt;</td>
<td>Standardised gas volume in dry cubic meters at STP and referenced to O&lt;sub&gt;2&lt;/sub&gt; or CO&lt;sub&gt;2&lt;/sub&gt;.</td>
</tr>
<tr>
<td>SO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Sulfur dioxide.</td>
</tr>
<tr>
<td>SO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Sulfur trioxide.</td>
</tr>
<tr>
<td>SO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>Oxides of sulfur (SO&lt;sub&gt;2&lt;/sub&gt;, SO&lt;sub&gt;3&lt;/sub&gt;, and H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;).</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Silica oxide.</td>
</tr>
<tr>
<td>STP</td>
<td>Standard Temperature and Pressure (0 °C and 101.325 kPa).</td>
</tr>
<tr>
<td>2,3,7,8-TCDD</td>
<td>2,3,7,8-tetrachlorodibenzo-p-dioxin.</td>
</tr>
<tr>
<td>t</td>
<td>Tonne.</td>
</tr>
<tr>
<td>t/hr</td>
<td>Tonnes per hour.</td>
</tr>
<tr>
<td>T&lt;sub&gt;(r,t)&lt;/sub&gt;</td>
<td>Raw meal temperature.</td>
</tr>
<tr>
<td>T&lt;sub&gt;i&lt;/sub&gt;</td>
<td>Initial meal temperature.</td>
</tr>
<tr>
<td>T&lt;sub&gt;∞&lt;/sub&gt;</td>
<td>Gas temperature.</td>
</tr>
<tr>
<td>TEF</td>
<td>Toxic equivalency factor.</td>
</tr>
<tr>
<td>TEQ</td>
<td>Toxicity equivalent of dioxins or furans to 2,3,7,8-TCDD, or PAHs to BaP.</td>
</tr>
<tr>
<td>TCDD/F</td>
<td>Tetrachloro dibenzo –p dioxin</td>
</tr>
<tr>
<td>TDF</td>
<td>Tire derived fuel.</td>
</tr>
<tr>
<td>TSP</td>
<td>Total suspended particulate.</td>
</tr>
<tr>
<td>TVOC</td>
<td>Total volatile organic compounds.</td>
</tr>
<tr>
<td>TW</td>
<td>Terawatt (10&lt;sup&gt;12&lt;/sup&gt; watts)</td>
</tr>
<tr>
<td>TWh</td>
<td>Terawatt hour (1 TWh = 3.6 PJ).</td>
</tr>
<tr>
<td>UMEF</td>
<td>Unit mass emission factor (analytical) for cement manufacturing.</td>
</tr>
<tr>
<td>UN</td>
<td>United Nations.</td>
</tr>
<tr>
<td>UNEP</td>
<td>United Nations Environmental Programme.</td>
</tr>
<tr>
<td>UNFCCC</td>
<td>United Nations Framework Convention on Climate Change.</td>
</tr>
<tr>
<td>US$</td>
<td>United States dollar.</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>USEPA</td>
<td>United States Environmental Protection Agency.</td>
</tr>
<tr>
<td>VDZ</td>
<td>Verein Deutscher Zementwerke.</td>
</tr>
<tr>
<td>VM</td>
<td>Volatile matter.</td>
</tr>
<tr>
<td>vol.%</td>
<td>Percentage by volumetric basis.</td>
</tr>
<tr>
<td>WBCSD</td>
<td>World Business Council for Sustainable Development.</td>
</tr>
<tr>
<td>WCA</td>
<td>World Coal Association.</td>
</tr>
<tr>
<td>WHO</td>
<td>World Health Organisation.</td>
</tr>
<tr>
<td>WMO</td>
<td>World Meteorological Organisation.</td>
</tr>
<tr>
<td>wt.%</td>
<td>Percentage by weight basis.</td>
</tr>
<tr>
<td>Zn</td>
<td>Zinc.</td>
</tr>
</tbody>
</table>
Acknowledgments

As the thesis submitted includes the research work carried out, I’d like to use the opportunity to express my appreciation to many of those involved. First and foremost, I would like to thank my primary academic supervisor Professor Igor Agranovski for encouraging me to pursue this research, and for his continual contributions of guidance and knowledge throughout its duration. The support gained from Professor Igor Agranovski has provided my understandings greater than that of any prescribed text.

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A special thank you is necessary to Doctor Andrew Chan, Doctor James Ness and Associate Professor Steven O’Keefe for their constructive feedback and recommendations on previous research materials. I would like to also thank the industrial personnel whom were exposed to my inquisitive conversations regarding cement manufacturing, process parameters and co-incineration.

Lastly, but by no means least, I would like to give a dear thank you to my wife and our children who have given me the ever-needed support and understanding towards my pursuit of this research.

This thesis is dedicated to my loving family, Maria, Cody, Lochlainn and Aoifè.
List of papers associated with the Thesis published during candidature


Chapter 1: Introduction

The focus of this thesis is to study the effects of co-incinerating different alternative derived fuels within several cement kilns operating to under normal conditions. This chapter describes the background and its problem statement, and the thesis objectives, approach and structure.

1.1 Background

Cement is produced on a global scale as a fundamental binding ingredient for the construction and development of infrastructure. As cement is the second most consumed material worldwide, the global rate of cement production has increased from 0.58 billion tonnes in 1970, to 3.1 billion tonnes in 2010, and its predicted demand is to reach 6.1 billion tonnes in 2050 (Cembureau, 2010; CSI, 2012; Holcim-GTZ, 2011; USEPA, 2010). Its’ manufacture from limestone (CaCO$_3$) is both a resource and energy intensive industry, which globally demands for 9% of industrial energy use (or 2% of primary energy use) and is accountable for 5-6 vol.% of global CO$_2$ emissions (IEA, 2007a; Worrell et al., 2008). Localised energy demands in some developing countries can be as high as 12 or 15% (Ail et al., 2011; Aranda-Usón et al., 2013), making it a highly-demanding consumer which can only intensify as global population and cement production increases.

In general, cement manufacturing requires $1.2 \times 10^7$ terawatt hours (TWh) of electrical energy, mainly consumed by grinding, and accounts for 30-40% of the total operating costs (Rasul et al., 2005). The thermal energy consumed is due to staged, intensive heating of raw meal for its chemical formation of clinker within the rotary kiln. The two-main pollutant-generating components of the process is the release of CO$_2$ bonded to limestone-magnesium carbonate, and the combustion of carbonaceous fuels for generating electricity and process needs (Bhatt et al., 2004, CIF, 2005; EIPPCB, 2013; IEA, 2007a; Neuffer and Laney, 2007).

Endothermic reactions required to pyro-process 1 tonne of cement (from 1.135 tonne of CaCO$_3$) use between 1.8 to 3.0 gigajoules (GJ) of thermal energy, and yields an equal tonnage release of CO$_2$ into the atmosphere. Of this tonnage, formation is primarily from calcination (55%); fuel combustion (35%); and 10% for other processes (Cembureau, 1999; ECOFYS, 2009; EIPPCB, 2013; Holcim-GTZ, 2011; IEA, 2010a; Willitsch et al., 2003). Traditional fuels used for combustion have largely been carboneous fossilised
resources (such as coal, petroleum coke or oil), with tests showing most incombustible matter being encompassed into the clinker product without compromising its quality characteristics or conformance with rigid engineering and testing specifications (Karstensen, 2004a; Venta, 2011).

With an increasingly stable human population growth from 3.7 billion to 7 billion people during 1970 to 2010, there is no imminent relaxation on cement production demands as the United Nations (UN) confidently projects 9.6 billion people in 2050 (Figure 1.1). Of this population growth, the expansion of urbanisation will also increase from 3.5 billion to 6 billion people between 2010 and 2050, requiring an additional 80% more energy (Cembureau, 2013) and providing extra stress to limited resources and climate change mitigations.

Figure 1.1: Historical and forecasted cement production overlaid with global population growth (Source: UN, 2013; Alsop, 2014).

Statistics for global cement production in 2014 was estimated to 4.18 billion tonnes (as seen in Figure 1.1), with a constant annual increase rate of 2.5 wt.% over numerous previous productions (USGS, 2015). This is predominately seen to be consumed by the industrialised growth in developing countries of Asia, with China (59.8% share) and India (6.7% share) currently being the largest market manufacturers (Figure 1.2) (Degré, 2014; EIPPCB, 2013; Madlool et al., 2011, 2013; Szabó et al., 2006; USGS, 2015). With a UMEF of 1.0, future emissions from current cement manufacturing practises is therefore set to double by 2050 (Alsop, 2014; EIPPCB, 2013; IEA, 2007a; Karstensen, 2007; Madlool et al., 2011; USEPA, 2010; Willitsch et al., 2003).
Country & cement production (million tonnes)

<table>
<thead>
<tr>
<th>Country</th>
<th>Production (Mt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>China</td>
<td>2500</td>
</tr>
<tr>
<td>India</td>
<td>280</td>
</tr>
<tr>
<td>USA</td>
<td>83</td>
</tr>
<tr>
<td>Turkey</td>
<td>75</td>
</tr>
<tr>
<td>Iran</td>
<td>75</td>
</tr>
<tr>
<td>Brazil</td>
<td>72</td>
</tr>
<tr>
<td>Russia</td>
<td>69</td>
</tr>
<tr>
<td>Saudi Arabia</td>
<td>63</td>
</tr>
<tr>
<td>Vietnam</td>
<td>60</td>
</tr>
<tr>
<td>Indonesia</td>
<td>60</td>
</tr>
<tr>
<td>Other</td>
<td>525</td>
</tr>
<tr>
<td>Japan</td>
<td>58</td>
</tr>
<tr>
<td>Egypt</td>
<td>50</td>
</tr>
<tr>
<td>Republic of Korea</td>
<td>48</td>
</tr>
<tr>
<td>Thailand</td>
<td>42</td>
</tr>
<tr>
<td>Mexico</td>
<td>35</td>
</tr>
<tr>
<td>Pakistan</td>
<td>32</td>
</tr>
<tr>
<td>Germany</td>
<td>31</td>
</tr>
<tr>
<td>Italy</td>
<td>22</td>
</tr>
<tr>
<td>Other</td>
<td>525</td>
</tr>
</tbody>
</table>

**Figure 1.2:** Counties of world cement production in 2014 (Source: USGS, 2015).

Recent reports by the Intergovernmental Panel on Climate Change (IPCC) (2007) identify that the target 450 ppmv carbon dioxide (CO$_2$) limit (referred to as 450 Scenario) which results in the preferred global mean temperature rise of 2.0-2.4 $^\circ$C, will only be achieved if current trends of energy consumption and unit mass emissions are acted upon with a 50-80% reduction (2000 equivalent CO$_2$ levels) by 2050. With the global amount of CO$_2$ from cement manufacturing being almost 2 gigatonnes (Gt) in 2010, the scenario expectation is that current practises will inadvertently increase to 2.4 – 2.9 Gt CO$_2$ by 2050 (Goisis, 2014; IEA, 2010a).

With the increasing establishment of environmental policies over the past few decades, pollutant-reduction and waste management challenges have recently been focused to key source sectors (including cement industry) and what actions are required (Cembureau, 2013). Many of these coincide with the urgently prompted success factors as stated by the International Energy Agency (IEA) 2050 CO$_2$ emission reduction roadmap (Figure 1.3), which will aid future reduction efforts in being achieved. Here the IEA idealise that significant CO$_2$ emissions can be mitigated through end-use fuel switching and efficiencies. This achievement has also been heavily studied by academics, international agencies and organisations (Herat, 1994; IEA, 2007a and 2010a and 2010b; Ke et al., 2012; Mikulčić et al., 2013a; Worrell et al., 2008), concluding that the cement industry has the highest potential to integrate energy savings (28-33%), reduce pollutant formation by thermal destruction, and reverse the contributions of CO$_2$ emissions (480-520 Mt CO$_2$/yr) by a quarter through four techniques, one of which is the co-incineration of alternative derived fuels (ADF).
Figure 1.3: Predicted CO₂ emissions from cement production (Source: IEA, 20010a).

These ADFs are considered in the context of energy-containing material or by-product which is no longer needed, and can be considered and used. The benefit of this is not only bonds the fuels’ residual inorganic element to the clinker crystal, but also reduces a CO₂ unit mass emission factor (UMEF)¹ equivalent value of 0.16 kilograms per tonne of clinker produced (Ke et al., 2012). With the industry leveraging off decades of experiments and testing with waste co-incineration, several countries have successfully permitted up to 83% of plant energy needs through the fuel substitution of waste oils, solvents, tyres, plastics, wood, hazardous waste and by-products, meat and bone meal (MBM), sewage sludge or refuse derived fuels (RDF) (Rahman et al., 2013 and 2015; WBCSD, 2010). Mokrzycki et al. (2003), Nielsen (2012) and Nørskov (2012) highlight the advantages of this concept to include:

1. The fuel being CO₂-neutral (either partially or completely);
2. Production costs are reduced from resourcing convention fuels, while waste from other industries are being recycled; and
3. High gas-material temperatures and residence time within the process initiate favourable mechanisms that can suppress the generation of harmful pollutants (e.g. chlorination of PCDD/F) or its entrapment into the clinker product.

1.2 Problem Statement

The concept of utilising alternative fuels is greatly exercised within the manufacturing industries of Europe whereby an 83% thermal substitution rate can be achieved by

¹ UMEF is the mass emission of air pollutant per unit of clinker produced.
utilising a range of low-carbon, combustible material. It is here whereby both policy makers and cement companies have integrated change over many years to demonstrate a 13 vol.% CO$_2$ emission reduction from 1990 to 2011 (Cembureau, 2014). However, science and caution must prevail as optimising the co-incineration of fuel alternatives is not straightforward and the limiting factors for all possible waste types (whether hazardous or not) has not completely been evaluated. Understandably, any industry involved in hazardous waste co-incineration without supporting evidence and valid conclusions can inherently be of concern as they are likely to contain or generate other air pollutants.

The integration of alternative fuels into this process system is however not so simple, with the final amount of fuel-energy required being dependent on the receiving material quality, process stability and efficiency, fuel acceptance, clinker specifications, and air emission limitations. As the chemical and physical properties of alternative fuels can differ to conventional fuels, several authors (Ariyaratne, 2014a; del Mar Cortada Mut, 2014; Nielsen et al., 2011; VDZ, 2009) identify that its substitution within an existing designed plant can have one or more consequences (Figure 1.4) namely:

- Generate products of incomplete combustion (PIC).
- Direct contact of raw meal with the fuel, affecting its calorific value (CV).
- Incomplete co-incineration of fuels containing relatively larger particles.
- Variability or instability of the stoichiometric ratio, based on fuel heating values, composition and hydrogen-carbon ratio.
- Increased gas velocities, the circulation of blockages or pollutant-forming catalysts (e.g. moisture, ash, sulfur, chlorine, and alkali metal species).
- Reduction in heat transfer, effecting material temperatures, calcination and clinkerisation.
- Reduced clinker production rate.
- Substitute generation of air pollutant(s) over the avoidance or complete destruction of other undesirable pollutant(s).
- Increased costs to operations or clinker production due to a combination of the above negative impacts.
To counterbalance some of these undesirable effects, existing plants have upgraded its process or equipment (e.g. kiln burners, fuel handling and feeding systems) and successfully shown through experimental trials, the reduction of operational difficulties. However, given its global position and lengthy participation within the Organisation for Economic Co-operation and Development (OECD), historical trial burns within Australian cement plants have been somewhat remained limited with governmental acuity of organic fuel substitution, waste reduction benefits and the subsequent air quality emissions (IEA, 2010b). This, in-turn, does not benefit cement plant operators to promote alternative fuel optimisation whilst complying with stringent emissions limits using best management practises (BMP) and best available techniques (BAT).

Regardless of international trials and agreements on the use of ADF (Baier, 2006; Karstensen, 2004b; Karstensen et al., 2005 and 2006 and 2010; Pipilikaki et al., 2005; Schneider et al., 2011), contrasting viewpoints within Australia between industry, community and government remain at large, ultimately contributing to the country’s current fuel substitution of 6% (DCC, 2008; WBCSD, 2010). Herat (1994) highlighted the problem several decades ago, and the continuation of opposing action groups appear
to extend the delay of utilising other opportunistic and compatible materials. This results in the current industry practise to remain utilising readily available carbonaceous fuels, and thus allowing for this co-incineration, energy conservation and emission reduction strategies not to be completely capitalised (Guajardo, 2014; Venta, 2011).

As some technical publications (Akkapeddi, 2008; Rovira et al., 2010, Schuhmacher et al., 2009) and emissions inventories (DCC, 2008; DIICCSRTE, 2013; Lei et al., 2011) only identify air pollutants to be particulate matter (PM), CO, NO\textsubscript{x} and SO\textsubscript{2}, information gaps currently exist on the co-incineration of some readily-available fuel types (e.g. paper, wood waste, anode-carbon dust) and the analysis of other subsequent source pollutants (e.g. heavy metals, PCBs, “dioxin-like” PCBs (dl-PCBs)). Supporting this, the main objective of this thesis is to provide information towards this knowledge gap and the asterisk-questions raised in Figure 1.4, through the approach shown in Figure 1.5.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{research_approach.png}
\caption{Overview of the research approach.}
\end{figure}
This approach includes:

1. Evaluating combustion fuel characteristics;
2. Establishing baseline emissions of target pollutants from ten full-scale cement plants (labelled A to J) while operating under normal facility conditions;
3. Conducting experimental co-incineration trials with differing waste materials at these cement plants whilst performing emissions monitoring;
4. Investigate ADF properties on the generation (and emission) of CO₂ and other pollutants, and optimising of fuel substitution rates\(^2\) in relation to pollutant emissions and clinker production rates.
5. Use statistical modelling techniques to investigate which ADF properties mostly influence pollutant-forming mechanisms (aiding the suppression or destruction of pollutants); and
6. Use statistical modelling techniques to investigate which ADF properties mostly influence key operating parameters (including temperature, residence time, excess air) and clinker production rates.

However, the overall challenge currently faced is not only to identify optimal solutions which can sustain economic growth while reducing climate change emissions, but for them to be feasible and readily adaptable, therefore accelerating these effective changes. The degree to which sustaining economies enforce proper regulations on industry emissions, essentially varies from country to country.

### 1.3 Thesis Outline and Impact

Evidence shows the air quality emitted from cement manufacturing processes has improved in recent years, particularly through techniques and technology of air pollutant control devices (APCDs). A contributor towards this is the added regulatory pressure of local Environmental Protection Agency’s (EPA) and other governing bodies by implementing stricter limits on carbon and greenhouse gas emissions from the industrial sectors. With current real-world emissions’ already being borderline with regulatory limits, additional avenues towards the options for ADF usage, the effects of ADF on combustion and plant operating parameters, and the suitability of present pollution control technology needs to be delineate. This thesis aims to investigate the impacts of co-

\(^2\) Rates are proportionally substituted to the calorific value of the petroleum coal used
incinerating alternative fuels in cement plants, and signify which process factors influence the formation and emission of air pollutants from these fuel types.

1.3.1 Thesis objectives and structure

The thesis objective is to provide scientific-based knowledge on the reduction of air emissions from the co-incineration of alternative fuels during cement production. This is achieved through a combination of examining baseline and experimental investigations, coupled with mathematical modelling. The questions answered from this study on alternative fuel co-incineration, include:

1. What are the impacts on CO\textsubscript{2} and other air pollutants UMEF?
2. What emission rates are affected by an increased amount of substituted fuel?
3. Which fuel properties influence combustion characteristics and pollutant-forming mechanisms?
4. Which key operating parameters are impacted from fuel substitution, and what fuel properties influence these effects?
5. What are the impacts to the rate of clinker production, and are any bottlenecks formed?

The knowledge obtained from this thesis may be used in cement plant design considerations to adopt alternative fuels characteristics for achieving optimal combustion conditions, to examine the feasibility and suitability of alternative fuel types to an existing cement plant, and to support regulatory and local community acceptance with its use. The thesis also provides several possible reasons for the negative impacts on clinker production rate (Load), thus supporting other presently-published literature.

The co-incineration component of this thesis has focused on process parameters and mechanisms which influence the formation of pollutants and incomplete combustion. The strategy is that firstly, Chapter 2 provides background information to the preheater-precalciner (PH/PC) kiln system process and key mechanisms, and which conditions influence, generate and control air pollutants. In developing emission-minimising strategies, research considerations include the effects of staged-process temperature, residence time, turbulence, excess oxygen and mixing ratios, fuel-containing catalysts, and fuel-sourced contaminants.

Chapter 3 provides a review on fuel characteristics currently used, available or being investigated within this study, highlighting where these characteristics relate to the above-
mentioned parameters. Chapter 4 provides the research methodology and design for the thesis (as they relate to Chapters 5, 6 and 7), including a correlation of the key operating parameters. Field monitoring and laboratory analysis methodologies are detailed.

Chapter 5 quantifies gaseous pollutants during normal clinker production and with the co-incineration of alternative fuels, while discussing factors of its formation and influence through multi-variance mathematical modelling. Gaseous pollutants of specific interest include CO₂, carbon monoxide (CO), nitrogen oxides (NOₓ, expressed as NO₂), sulfur oxides (SOₓ, expressed as H₂SO₄), and volatile organic compounds (TVOCs) which includes benzene, toluene, xylene (BTX).

Under simultaneous process and combustion conditions, Chapter 6 describes the further monitoring of particulate and trace species (PM, halides and halogens, heavy metals), while Chapter 7 examines the monitoring of inorganic pollutants (PAHs, PCDD/F, PCBs, dl-PCBs). Within each chapter, the empirical models are used to identify existing impacts to key characteristics, pollutant-influencing parameters, and to the clinker production rate.

Chapter 8 summarises the key operating characteristics shown to influence pollutant-forming mechanisms, and Chapter 9 discusses the most effective alternative fuels to pollutant emissions and clinker production rate. Chapter 10 contains the overall conclusions on optimising the co-incineration of alternative fuels within cement plants. Recommendations for further work are provided.
Chapter 2: Literature Review

2.1 Introduction

As shown in Chapter 1, this thesis seeks to provide evidence on factors that influence the co-incineration of alternative fuels for thermal energy whilst manufacturing cement clinker, and to identify any emission reduction of air pollutants. This chapter provides a general overview of the cement manufacturing process, and the implications of fuel use on its air emissions. Firstly, a short discussion is provided on the characteristics of cement plants commonly used in Australia is provided, followed with a brief overview of the impacts and statutory limitations on air emissions. Subchapters 2.5 and 2.6 review the mechanisms which influence the generation and emission of air pollutants, and a final discussion is provided on the technology currently used for post-combustion pollutant control.

2.2 Background

2.2.1 Cement production and chemistry

Cement manufacturing has long revolutionised from the historic dome or kiln shafts, with the main ingredients being limestone, sand, clay, shale, iron ore and up to 30 other raw materials. Confined within, and defined to, the CaO-SiO$_2$-Al$_2$O$_3$ ternary phase diagram (Figure 2.1), the hydraulic and pozzolanic characteristics of these elements ultimately allows for the binding of the clinker material its final cementitious form (Degré, 2014).

![Figure 2.1:CaO-SiO$_2$-Al$_2$O$_3$ ternary phase diagram (Source: Hewlett, 2004).](image)

Cement manufacturing begins with the energy-intensive mechanical crushing, drying and grounding of raw materials, of which contain oxides of calcium, silica, aluminium, and
iron (Fe). Further storage and blending of the powderised raw meal, physically prepares the mixture to a typical constituent ratio of 66 wt.% of calcium oxide (CaO) from limestone (CaCO₃); with up to 21 wt.% of silica oxide (SiO₂) and 5 wt.% of aluminium oxide (Al₂O₃) from sand, clays or shales; with 3 wt.% iron oxide (Fe₂O₃) from raw materials, and 5 wt.% other trace components (Alsop, 2014; CIF, 2005; Madlool et al., 2011; Worrell et al., 2001).

Where any deficiencies or variations in meal composition arise, this inadvertently can decrease kiln productivity and quality while increasing the overall fuel consumption and UMEF. It is also important that the stoichiometric ratio of alkalis at 1.5% is significant, as the effects of inorganic volatiles, sulfur, or chlorides can have a higher risk of operational problems such as blockages in the PH/PC tower or shell corrosion to the kiln (Aranda-Usón et al., 2013; Alsop, 2014; del Mar Cortada Mut, 2014; Deolalkar, 2009; IIP, 2013; Nielsen, 2012). The use of preheater (PH) exhaust to dry material in the raw mill aids energy efficiency to the plant, and scrubs out any sulfides or other acids within the flue gas.

The raw meal is transferred into a PH/PC tower and kiln system for staged combustion and carbonate decomposition (also referred to as pyro-processing). Within this PH/PC-kiln system, an induced draft fan (IDF) is used to draw hot flue gas from the kiln through the PH/PC tower in the opposite direction to the material flow, and provides some assistance to overcome considerable gas flow resistance (Neuffer and Laney, 2007). This allows for the raw meal and combustion gases to be in direct contact with each other, allowing their interaction. The clinker nodules are then moved from the kiln into the cooler for later blending, grinding and storage before being shipped off. This further stage of grinding product and additives to a fine powder (200 micrometres (µm)) is also energy intensive, accounting for about 35% of the plants’ electrical energy. An overview of the process is presented in Figure 2.2.

The chemical reaction phases (Figure 2.3) which transform the raw meal to clinker will typically occur between 700 to 1450 °C, with the final product composition generally being as shown in Table 2.1 (Taylor, 1997). Mastorakos et al. (1999) identify elements whereby subtle design and operation changes to the PH/PC-kiln system can affect the process’s energy requirements, clinker quality produced, and the air pollutants released.
Figure 2.2: General overview of a PH/PC-kiln cement plant (Source: IEA, 2010a).

Figure 2.3: Phase diagrams for cement clinker production (Source: Taylor, 1997).

Table 2.1: Main constituents for cement clinker (Source: Taylor, 1997).

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical name (and composition)</th>
<th>Nomenclature</th>
<th>Proportion [wt.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belite</td>
<td>Dicalciumsilicate ((CaO)_2\cdot SiO_2)</td>
<td>C_2S</td>
<td>15-30</td>
</tr>
<tr>
<td>Alite</td>
<td>Tricalcium silicate ((CaO)_3\cdot SiO_2)</td>
<td>C_3S</td>
<td>50-70</td>
</tr>
<tr>
<td>Ferrite</td>
<td>Tetracalcium aluminoferrite ((CaO)_4\cdot Al_2O_3\cdot Fe_2O_3)</td>
<td>C_4AF</td>
<td>5-10</td>
</tr>
<tr>
<td>Aluminate</td>
<td>Tricalcium aluminate ((CaO)_3\cdot Al_2O_3)</td>
<td>C_3A</td>
<td>5-15</td>
</tr>
</tbody>
</table>

2.2.2 Preheater

The PH/PC tower (Figure 2.4) is a 5-staged dry-process suspension preheater kiln with a precalciner vessel. The PH is a series of interconnecting cyclones and ducts specifically designed for the initial drying of immersed moisture (IM) and the heating of the raw meal
(from 100-750 °C) for approximately 2 minutes, prior to the precalciner (PC). As the raw meal is fed into the upper cyclone stages of the PH, it is caught in suspension of the hot flue gas and pulled into the first cyclone for further separation by centrifusion (Neuffer and Laney, 2007).

Figure 2.4: Process design and mass balance of PH/PC-kiln system.

Because the flow of feed is held suspended in the hot counter-flowing gas stream (of 400-650 °C), there is rapid heat transfer between gas and raw material, increasing the raw meal from 100–400 °C and causing the release of IM from clay-like substances. As the fast gas stream enters the PH tower, the material travels by gravity from the first-stage cyclone via a duct between the second and third-stage cyclones. The lower cyclones provide centrifuge to almost 80 wt.% of heated raw meal from the flue gas and supply the cyclone stage beneath. The oxygen (O₂) concentration in the PH is shown to vary, however it is generally low due to oxidising the raw meal and any influences on pollutant-formation (e.g. from pyrites, calcite or organic carbon) (Larsen, 2007; Taylor, 1997).
As the gas phase (containing the remaining solids) flows directly to the smaller double cyclones above, a further 95 wt.% of material is removed from it under reduction conditions (i.e. 5-10 vol.% O₂, 300 °C). By the time the raw meal leaves the PH, the material temperature (PHₚₜ) has increased to 650–750 °C, dehydrated and decomposed any clay minerals, oxidised any organic compounds which may be present, and decompose the limestone and magnesium carbonate (MgCO₃) into magnesium oxide and CO₂ (Neuffer and Laney, 2007). As raw meal generally contains sulfides and organic sulfur, when it moves through the PH it is predominately oxidised and moves within the flue gas stream. Process gas levels within the PH are closely monitored for changing temperature, O₂, CO NOₓ and TVOC (generally 1-80 mg/Nm³) levels.

2.2.3 Precalciner

The hybrid precalciner is a separate vertical vessel, positioned at the bottom of the PH/PC tower prior to the rotary kiln entrance (Figure 2.4), for the complex chemical and physical reactions to occur between the gas-solid phases (Zhang et al., 2011). Some studies (CIF, 2005; Neuffer and Laney, 2007) indicate the constant monitoring and control of flame temperature, pressure, gas and feed rates at this stage helps to limit the formation of fuel and thermal NOₓ, however Commandré et al. (2005) have indicated the PC design can generate significant fuel NOₓ quantities. The PC is fed with secondary fuel which does not need to be of equal quality to the kiln burner fuel, partially due to the PC’s increased gas residence time. Predominantly coal is used as secondary fuel, however, most other solid or liquid fuels could be considered including waste tyres, oil and materials (Neuffer and Laney, 2007).

Above this feed location is the NOₓ reducing zone and where the combustion gases (known as tertiary air, at 21 vol.% O₂) drawn from the pyro-processing (clinker cooling) system is introduced. The mixing and combustion of these in the oxidizing zone leads to an increase in temperature, gas-solid heat exchange, decomposition of raw meal, and the dilution to about 14 vol.% O₂. The extent of these have a direct relationship to the quality of clinker, energy consumption and emissions. These are controlled through the composition and mass flow of the raw meal, secondary fuel and tertiary air.

Additionally, as combustion occurs at a PCₚ of 750–900 °C, low-carbon based fuel with a low CV is quite capable of delivering enough energy to calcinate the limestone, and this is where the greatest opportunity to supplement with ADFs (as shown in EIPPCB (2013))
and Karstensen et al. (2005)). As the process utilises 60% of its fuel consumption in the PC, the opportunity for injecting fuel at this stage can suppress NOx formation as the calcining fuel is initially burned under reducing conditions and then burned further in the kiln at a reduced oxidised condition. Even though thermal NOx may be minimal, the opportunity to generate fuel NOx is therefore of significance. Once the material leaves the PC combustion zone, it has achieved 90–95% calcination and with CaO being the remaining material component, its weight is reduced by 30%. Mikulčić et al. (2013a) summarises the stoichiometric reaction within the PC vessel as:

\[
\text{Energy} + \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 + 178 \text{ kJ/mol} \quad (2.1)
\]

The material and gas stream is moved to a final cyclone, where centrifusion sends the calcined feed into the rotary kiln entrance, and the separated flue gas remains in the vessel with PCgt ranging between 850-1,200 °C. A correlation of experimental PCgt and precalciner material temperatures (PCmt) is shown in Figure 2.5.

![Figure 2.5: PCgt and PCmt during combustion of petcoke, PCgt = 900 °C, S1 = 0.8 (Source: Commandré et al., 2005).](image)

At this stage, Belite is further formed with free CaO and quartz SiO₂ (as seen in Figure 2.3) through:

\[
2 \text{ CaO} + \text{SiO}_2 \rightarrow 2 \text{ CaO-SiO}_2 \quad (2.2)
\]

### 2.2.4 Rotary kiln

Details of rotary kilns tend to vary across manufacturing plants and are greatly dependant on the raw meal feed rate (Feed). However, as a counter-flow heat exchanger, they are generally confined to as a cylindrical metal tube, approximately 60-80 meters long and
3.5-5 meters in diameter. These are typically sloped to a 3-4° incline, rotate at 1.5-3.5 revolutions per minute, and are lined inside with refractory bricks. The kiln rotation is supported and driven by structural elements which allow for the riding rings to engage with steel rollers, with another set is positioned downstream (Saidur et al., 2011a). The slow rotation of an inclined kiln causes the material to move towards the kiln’s lower, hotter end.

Entering the kiln from the last cyclone of the PH/PC tower, the mass flow of feed material travels the kiln chamber length for about 30 minutes while being exposed to a combination of friction and increasing flue gas temperatures (Kg). While monitoring the kiln gas levels (including temperature, O₂, CO and NOₓ), the slight inclination, slow rotation and extreme heating conditions of the kiln help nearly achieve complete destruction of organic pollutants which are generally resistant to loading and temperature fluctuations (Cembureau, 2009; Neuffer and Laney, 2007).

Located at the kiln’s downward end, the Pillard Rotaflam burner ignites high calorific fuel (general operation designs require at least 30-35 megajoules per kilogram (MJ/kg)) to produce a constant burner flame temperature (Kᵣ) profile of 1,600 - 2,000 °C at a residence time (Kᵣ,n) of 8 seconds. The function of providing this profile is so that the necessary forms of energy is available for the clinker reactions to occur. The conventional combustion of natural gas, process gas or powdered coal through the burner is sustained by regulating the gas flow rate with (or without) air to achieve the required flame conditions and level of excess air (Oₑ) (Karstensen et al., 2005; Neuffer and Laney, 2007). The normal air introduced at the flame supports the combustion and calcination actions within the kiln, and is significantly diluted to 2-5 vol.% O₂ as it enters the PC.

As the feed material travels through the rotary kiln and approaches the sintering zone, about 20 wt.% of material is molten and the clinker temperature (Loadₘₜ) is required to reach at least 1,400 °C for it to undergo its final chemical reactions in the combustion zone (Kₘₜ preferred to be about 1,800 °C at 3 vol.% O₂) (Herat, 1994). Alite (C₃S) is further formed here from belite (C₂S) and free CaO:

\[
2 \text{CaO} \cdot \text{SiO}_2 + \text{CaO} \rightarrow 3 \text{CaO} \cdot \text{SiO}_2
\]  
(2.3)

Through initial cooling from the kiln, Ferrite (C₄AF) and Aluminate (C₃A) crystals are formed by the following reactions (Herat, 1994; Hewlett, 2004; Neuffer and Laney, 2007; Taylor, 1997; USEPA, 1995a; Willitsch et al., 2003):
When the final cement product is mixed with water, these four Bogue compounds react to form most of the cementitious configuration. As cement kilns are complex, the near-complete destruction of pollutants is greatly derived by numerous parameters such as fuel CV, combustion gas and meal temperatures, flame temperature and residence time, fuel and meal compositions, Oe, IM content, and air-fuel mixing (Boubel et al., 1994).

2.2.5 Clinker cooler and storage

Once the clinker has passed the combustion zone of the rotary kiln, the Load$_{int}$ is cooled to about 1,250 °C before being discharged from the kiln into the clinker cooler. The purpose of the clinker cooler is to recover heat from the hot clinker, and to cool down the clinker for about 15-30 minutes in preparation of storage or grounding.

Within the clinker cooler, ambient air is induced through the clinker bed to significantly reduce the Load$_{int}$ down to about 100 °C. Recovered hot air from the clinker cooler (via the kiln hood) is transferred as combustion air back to the kiln (called secondary air) or as combustion air in the precalciner (called tertiary air). An advantage of recirculating this recovered heat back to the process has shown to reduce chlorine and sulfates, whilst providing an improved efficiency on thermal energy and fuel usages due to limiting the need to regenerate the heat from combustion (Neuffer and Laney, 2007).

2.2.6 Pyro-processing overview

From the above, Table 2.2 provides an overview of temperature and residence time (for gas and material), and gas O$_2$ concentration in modern cement plants.

<table>
<thead>
<tr>
<th>Table 2.2: Overview of temperature, time and O$_2$ vol.% within a modern PH/PC-kiln.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gas</strong></td>
</tr>
<tr>
<td>Temperature °C</td>
</tr>
<tr>
<td>Residence time [s]</td>
</tr>
<tr>
<td>O$_2$ [vol.%]</td>
</tr>
<tr>
<td><strong>Material</strong></td>
</tr>
<tr>
<td>Temperature °C</td>
</tr>
<tr>
<td>Residence time [s]</td>
</tr>
</tbody>
</table>
2.2.7 **Induced draft fan**

The induced draft fan provides both the necessary combustion air to the kiln burner and the energy required overcoming material resistance to the gas flow. Secondary and tertiary air is provided to the kiln burner and PC, respectively, from the clinker cooler for heat recovery. Once passed through the PH/PC-kiln tower, the flue gas is directed through the raw material mill and coal mill, prior to undergoing the selected APCD (such as fabric filters or electrostatic precipitators, discussed later in subchapter 2.7) and exiting the main stack. Cement kiln dust (CKD) is a fine-grained by-product of the process which is removed and would otherwise be discharged. The unit mass emission of numerous parameters is monitored through an on-line continuous emission monitoring system as the flue gas exits the stack, specifically for temperature, O₂, CO, CO₂, NO, NO₂, SO₂, hydrogen chloride (HCl), water vapour and TVOCs. But what are the implications of these and other emitted pollutants.

2.3 **Impacts of Air Pollutants**

As combustion refers to the exothermic oxidation of fuel and air for the development of heat and energy, the ideal products from a stoichiometric combustion reaction would be CO₂ and water, along with diminutive changes to trace substances such as nitrogen or sulfur. However, with the combustion of various fuels being largely dependent on several variables (e.g. fuel composition, equipment, technology, process operations, and combustion conditions), the realistic emanation can also include particulate and gaseous contaminants.

The determination of air pollution concentrations in compliance with an acceptable quality limit on the surrounding public health and wellbeing is both judgemental and debateable. This poses the question of what health damage is acceptable. For this, we need to critique the associated environmental and health impacts of gaseous pollutants (CO₂, CO, NOₓ, SOₓ, TVOCs), particulate and trace pollutants (halogens, metals), and inorganic pollutants (PAHs, dioxins, PCBs) released from cement manufacturing.

2.3.1 **Gaseous pollutants**

So why are we concerned with the effects of greenhouse gas and other pollutants? As a well-established and recently debated topic, the key concern with greenhouse gas (GHG) emissions is the impact on global climatic changes, as well as human health and socio-
economic well-being. When greenhouse gases\(^3\) are put into the atmosphere and increase the current concentrations, the predisposition traps more of the planets’ radiating solar energy into the atmospheric blanket (Baukal, 2004). This absorption of infrared radiation in-turn heats up the planet’s atmosphere and surface, as seen in Figure 2.6.

![Diagram of the Greenhouse Effect](image)

**Figure 2.6:** Atmospheric pollution and greenhouse effect (Source: Baukal, 2004).

Even with the recent decades of raised global awareness, international negotiations and the trifling intervention of greenhouse gas emission and its effects to climate change; the reality is that we utilise more energy and carbonaceous fuels than any other time in history. The World Metrological Organisation (WMO) identifies CO\(_2\) account for 82 vol.% of GHG effects, regardless of its global warming potential (GWP) (Damtoft *et al*., 2008; Guajardo, 2014; World Bank, 2014). Queiroz Lamas *et al.* (2013) note the relativeness of other key pollutants to CO\(_2\)’s GWP, also referenced as CO\(_2\) equivalent (CO\(_2\)\(_e\)) based on mass units of pollutant released per fuel usage, can be seen by equation 2.6.

\[
\text{CO}_2\!\!\!\!_e = \text{CO}_2 + 1.9\!*\!(\text{CO}) + 25\!*\!(\text{CH}_4) + 50\!*\!(\text{NO}_x) + 80\!*\!(\text{SO}_2) + 67\!*\!(\text{PM}) \tag{2.6}
\]

This is further supported with recent measurements by the WMO identifying that of the hottest 15 years ever recorded, 14 of them have occurred within the 21\(^{st}\) century. Furthermore, with last year recorded as the hottest year due to the average global air temperature recorded at 0.57 °C above the long-term 1990 reference period (of 14 °C), it is expected that global warming will continue in the immediate future (WMO, 2014).

More recently, the monthly average CO\(_2\) concentration for March 2015 was reported by WMO (2015) to have globally reach and exceed 400 ppmv for the first time. Measurements by the National Oceanic and Atmospheric Administration (NOAA) at the

\(^3\) namely water vapour, CO\(_2\), NO\(_x\), methane (CH\(_4\)) and ozone
Mauna Loa Observatory in Hawaii have shown dry molecular air being recorded at 400.8 ppmv CO₂ (Figure 2.7), which have increased over the past half-century, with more predominate increases being within the past two decades (Figure 2.8). NOAA (2015) further identifies this with significant scientific evidence showing the combustion of carbon-based fuels (along with other human activities) is primarily responsible, and that time to make an effective change is constantly running out.

Figure 2.7: Historical and recent monthly average CO₂ concentrations at Mauna Loa Observatory, Hawaii (Source: NOAA, 2015).

Figure 2.8: Decadal average (horizontal bar) and annual average (vertical bar) growth rates of CO₂ at Mauna Loa Observatory (Source: NOAA, 2015).

With various types of research conducted on the generation and release of CO₂ emissions from clinker production, the CO₂ UMEF is shown to vary dramatically between plants and due to fuel use. Deja et al. (2010) and Damtoft et al. (2008) identifies that cement plants around the world generally emit a total CO₂ UMEF between 0.8-1.0 (Figure 2.9), with thermal fuel consumption remaining consistently at about 40%, giving an average fuel-derived CO₂ UMEF between 0.3-0.45 (Figure 2.10).
With the general concentration of CO₂ from cement plants being high (about 25 vol.%, dry basis) and influences of its generation being predominately from carbonate decomposition, the substitution of raw materials with a high CaO-content would be beneficial (Barker et al., 2008). However, the availability and kiln-suitability of these materials are sometimes relatively limited or not locally / readily available.

Although the true effects of increased GHG isn’t completely known, recent global experiences include more extreme and ad hoc weather conditions with more rainfall, longer and drier droughts, and stronger storms (Worrell et al., 2001). The World Bank (2013) report based off current conditions show that a 2 °C rise will cause unusual heat extremes in most areas, decrease in tropical cyclones, severe droughts within Africa, a global sea-level rise towards 70 cm, significant losses in agricultural pastures, severe flooding, increased risk to human health, and unnatural stresses to aquatic and terrestrial ecosystems. The environmental effects from global warming is increasingly different throughout the regions, and this adds additional strain to an already-challenged subject
which can only get worse. As an ongoing population growth is only going to increase the demand for cement production, we are therefore within a pivotal period of history whereby the innovative and decision-making avenues explored (and integrated) will be the foundations on future emission-reducing predicaments.

With this, the economic advantage of acting upon technical endorsements specific to emission reduction, is that that technological and social shifts will expand within economic societies, sub sequentially supporting low-carbon objectives and business economic growth. These shifts are evidently significant to recent legislative and economic changes within Europe and Canada, both of who are investing in polluting less, wasting less, and make more productive use of energy and natural resources (EC, 2001; Environmental Registry, 2015).

The Global Commission on the Economy and Climate (GCEC), an international initiative to analyse global economic benefits and costs associated with climate change approaches, has estimated about US$6 trillion per year is to be invested on short-term infrastructure developments (NCE, 2014), and that much of this will shape the future segregation of economic concerns and the challenges of emission reduction. This investment of low-carbon futures can be greatly supported by leading and developing economical nations (such as China, India and Europe), particularly where the localised CO$_2$ emission levels are more extensive. An example of opportunity is China, whereby 57 vol.% of CO$_2$ emissions is accounted from its clinker production (Lei et al., 2011; Szabó et al., 2005 and 2006). The human health effects of a moderate, prolonged CO$_2$ exposure can cause acidosis and adverse effects on a body’s calcium phosphorus metabolism, resulting in increased calcium deposits in soft tissue. Initial exposure to CO$_2$ will cause drowsiness, increase blood pressure and heart rate, and reduced hearing. Extended exposure causes stimulation of the respiratory centre, dizziness, difficulties with breathing, headaches, and eventually tremors leading to the loss of consciousness (De Nevers, 2000).

As an intermediate product of under-stoichiometric combustion, the relative proportion of CO released is not as high as CO$_2$, however the associated health risks are vigilant (Baukal, 2004). Carbon monoxide is colourless and odourless, but can cause harmful health effects by combing with haemoglobin in the blood and reducing the oxygen delivery to the body’s heart, brain and tissues (Baukal, 2004). Low exposure to people who suffer from heart diseases can result in cardiovascular effects. Studies have shown
CO concentrations as low as 67 µg/Nm³ can affect up to 50 wt.% of the body’s haemoglobin.

As a product of solid fuel combustion, the study of NOₓ emissions has increasingly been studied over recent decades due its contributions to photochemical smog and acid rain (Wright and Boorse, 2011). Nitric oxide (NO) does not significantly affect human health, however, elevated levels of NO₂ causes damage to the mechanisms that protect the human respiratory tract (Colls, 2002). Nitrogen dioxide reacts with compounds in the atmosphere to form nitric acid (HNO₃), which are shown to effect breathing and respiratory functions, damage to lung tissue, and premature death (Baukal, 2004). With the low solubility of NO, the penetration of small nitric particles into the deep sensitive parts of the lungs can cause or worsen existing respiratory diseases. Epidemiological studies show the long-term exposure of NO₂ to asthmatic children can increase symptoms of bronchitis, along with the reduced growth function of a lung is linked to NO₂ concentrations measured in Europe and North America (Colls, 2002; WHO, 2006).

As gaseous SO₂ is highly soluble in mucosal fluids with a significantly low penetration of 1 % into alveoli surfaces (De Nevers, 2000), most guidelines had previously interlinked it with PM due to epidemiological studies undertaken on people exposed to a mixture of pollutants. Extensive studies by the USEPA (2009 and 2010) have correlated human health effects against the short-term exposure of SO₂ concentrations (20-100 ppbv), showing that asthmatics are more sensitive to the increasing effects of these concentrations. Long-term exposure is revelled to cause additional health effects of chronic bronchitis, heart disease or lung disease. In the American Cancer Society (ACS) studies, the WHO (2006) reported a significant association between mortality and SO₂ concentrations (mean of 18 µg/m³, highest of 85 µg/m³).

The impacts of TVOCs are known to be two-fold, firstly as a photochemical precursor to ozone production and secondly as some species have carcinogenic and mutagenic effects to humans (Colls, 2002; De Nevers, 2000). Benzene is a highly toxic compound where acute breathing exposure can cause drowsiness, dizziness, rapid heart rate, headaches, tremors and unconsciousness. Determined as a human carcinogen, the chronic effect of benzene travels through the blood supply targeting liver, kidney, lung, heart, and the brain. Damages to the bone marrow can decrease the generation of red blood cells, causing leukaemia and other blood cancers (USEPA, 2010). Toluene is a naturally occurring compound used in several industrial sectors, with its subsequent health impacts
been shown to include behavioural problems specific to the central nervous system and memory loss (De Nevers, 2000).

According to the International Agency for Research on Cancer (IARC), research and epidemiological studies into the causes of cancer identify criteria pollutant agents, mixtures and exposures to be that of Category 1 carcinogens. Agents of this group are *carcinogenic to humans* as supported by sufficient evidence of carcinogenicity in humans. The following trace and inorganic pollutants fall within this category.

### 2.3.2 Particulates and trace species

For particulate matter, studies (USEPA, 2010) have shown that respiratory problems occur because of inhalable particles (less than 10 µm) and fine particles (less than 2.5 µm), and it affects more people than any other pollutant. The main components of PM$_{10}$ and PM$_{2.5}$ can have sulfate, nitrates, ammonia, chloride, metals, and hydrocarbons. The mixture of solid and liquid, organic and inorganic pose great health concerns as they get deep into the lungs bronchioles, interfere with the gas exchange, and may dispose into the bloodstream (Baukal, 2004; Colls, 2002).

Scientific studies have linked chronic exposures of PM to contribute to the risk of developing cardiovascular and respiratory diseases, decreased lung capacity and function, aggravated asthma, development of chronic bronchitis, irregular heartbeat, non-fatal heart attack and strokes, and premature cancerous-death in people with lung or heart disease (Colls, 2002). Epidemiological evidence shows adverse effects of PM can occur following both short-term and long-term exposure. Long-term exposure has initiated the recommended concentrations due to significant effects of survival observed in the ACS study. From other various studies, WHO (2006) report the robust associations between long-term exposure to PM$_{2.5}$ and mortality rates. With the introduction of recent stringent emission limits and utility of BAT, studies have quantified the socio-economic effect of reducing contaminated PM$_{2.5}$, annually yields in the distinctive population avoidance of premature mortality cases, and the extensive reduction respiratory effects associated with doctor visits (20,650), hospital administration (1,740), lost work days (130,000), and restricted activity days (750,000) (USEPA, 2010).

Hydrogen halides and halogens are a process interest as the later reaction with water vapour can present corrosive acids (e.g. hydrochloric acid), however its brief exposure
can cause coughing and throat irritations, while high concentrations can impact upper respiratory tract, pulmonary edema, and circulatory system failure (USEPA, 2010).

For exposure to heavy metals, arsenic (As) and its compounds are potent poisons to the human adenosine triphosphate cells, which inhibit the energy-linked reduction of mitochondrial respiration and can lead in death from multi-organ failure. Acute exposures to beryllium (Be) can result in a pneumonia like disease that affects the respiratory system and minor lung deposits. Chronic exposure to Be and its compounds causes chronic beryllium disease, pulmonary and systemic granulomatous disease, and lung cancer giving symptoms of fatigue, weakness, and breathing difficulties (Tillman, 1994). Exposure to cadmium (Cd) and its compounds can result in chemical pneumonitis (inflammation of lung tissue), pulmonary edema (fluid accumulation in the lungs), and carcinogenic cancer.

Mercury (Hg) and its compounds are extremely toxic and volatile elements which commonly exist in small impurities of solid conventional and waste fuels. Studies on the acute exposure of Hg from industrial airsheds show sufficient evidence of the causal relationship of sulfur deposition and increased Hg levels, subsequently contributing to chest pain, dyspnea, haemoptysis, and pneumonitis. Case control studies on chronic exposure showed carcinogenic effects as well as tremors, impaired cognitive skills, and sleep disturbance (USEPA, 2010). Nickel (Ni) and its compounds are also extremely toxic and evident that chronic exposures contribute to carcinogenic effects. It is evident in Figure 2.11 that most of the metal emissions trends for Queensland remain constant over the past decade.

![Emissions of Copper, Chromium (VI), Lead, Nickel and Zinc to Air – QLD](image1)

![Emissions of Cadmium, Chromium (VI), Mercury and Selenium to Air – QLD](image2)

**Figure 2.11:** Emission trends of metals for Queensland 2002-2007 (Source: EPA, 2008).

A health impact associated with the exposure of lead (Pb) results in distribution in the blood (reduces oxygen carrying capacity) and accumulates in the bones. Depending on the level of exposure, Pb can adversely impact the nervous system, kidney function, and cardiovascular system. From other key pollutants, Figure 2.12 shows a consistent trend.
in Queensland’s recent emissions, even with the adoption of technological advances. The second graph of air toxic emissions provide evidence the following criteria pollutants are present.


**Figure 2.12**: Emission trends of key air pollutants for Queensland 2002-2007 (Source: EPA, 2008).

### 2.3.3 Inorganic pollutants

Other pollutants of interest to this research are those that also have a detrimental and carcinogenic impact on human health, and include halogens, PAHs, dioxins and PCBs. As there is a significant number of PAHs released from combustion varying from non-toxic to extremely toxic, IARC have classified 48 PAH compounds likely to be carcinogenic to humans. From these, the USEPA have identified the possible formation of seven main PAH compounds where chronic exposure has identified carcinogenic, mutagenic, and teratogenic effect to humans, and therefore have specific monitoring considerations. These PAH compounds have a WHO (2005) toxic equivalency value are referenced to Benzo(a)pyrene (BaP-TEQ value being 1.0), and include Benzo(a)anthracene, Chrysene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Indeno(1,2,3-c,d)pyrene, and Dibenz(a,h)anthracene.

Persistent organic pollutants (POPs) mainly characterize polychlorinated dibenzo-\(p\)-dioxins and furans (PCDD/F) and PCBs as significant environmental pollutants and possible human carcinogens. Dioxins are naturally occurring compounds that consists of two benzene rings bridged by two oxygen atoms, whereas furans consist of two benzene rings interlocked by a single oxygen bridge and a single carbon-carbon bond, seen in **Figure 2.13**. The main carbon-carbon structure is substituted at different positions of the molecule (from 1-4 and/or 6-9 in **Figure 2.13**) by one or more chlorine atoms. PCBs are aromatic compounds formed such that the hydrogen atoms on the biphenyl molecule (two
benzene rings bonded together by a single carbon-carbon bond) may be replaced by up to 10 chlorine atoms (UNEP, 2001).

**Figure 2.13:** Chemical structure of PCDD/Fs and PCBs

From this, a total of 210 individual PCDD/F congeners have been identified (Table 2.3), arising from chlorine-counting homologue patterns of 75 PCDD congeners and 135 PCDF congeners. Of these, there are 17 congeners with chlorine atoms on the 2,3,7,8 positions, and have been declared by the North Atlantic Treaty Organisation (NATO) and the World Health Organisation (WHO) as compounds that exhibit toxicity (WHO, 2005). The most toxic dioxin congener is identified as 2,3,7,8-tetrachlorodibenzo-p-dioxin (referenced as 2,3,7,8-TCDD) which efficiently binds with cell receptor proteins, binding with the DNA, and disrupting the mechanisms for reproducing proteins. (Ahlborg *et al.*, 1994; Conesa *et al.*, 2008; Karstensen *et al.*, 2010; Pandelova *et al.*, 2006; Rivera-Austrui *et al.*, 2011, WHO, 2005).

**Table 2.3:** Number of possible PCDD/F congeners within each homologue group.

<table>
<thead>
<tr>
<th>Chlorine count</th>
<th>Homologue pattern</th>
<th>Number of congeners</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Monochloro</td>
<td>2</td>
<td>MoCDD/F</td>
</tr>
<tr>
<td>2</td>
<td>Dichloro</td>
<td>10</td>
<td>DiCDD/F</td>
</tr>
<tr>
<td>3</td>
<td>Trichloro</td>
<td>14</td>
<td>TriCDD/F</td>
</tr>
<tr>
<td>4</td>
<td>Tetrachloro</td>
<td>22</td>
<td>TCDD/F</td>
</tr>
<tr>
<td>5</td>
<td>Pentachloro</td>
<td>14</td>
<td>PeCDD/F</td>
</tr>
<tr>
<td>6</td>
<td>Hexachloro</td>
<td>10</td>
<td>HxCDD/F</td>
</tr>
<tr>
<td>7</td>
<td>Heptachloro</td>
<td>2</td>
<td>HpCDD/F</td>
</tr>
<tr>
<td>8</td>
<td>Octachloro</td>
<td>1</td>
<td>OCDD/F</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td>75</td>
<td>135</td>
</tr>
</tbody>
</table>

As an extremely persistent and non-polar compound, PCDD/F congeners specifically exhibit hydrophobic and lipophilic (fat-soluble) properties and this supports the ability to bio-accumulate in humans causing known immune and enzyme disorders, mutations, teratogens, and carcinogenic health effects (UNEP, 2001; Xu *et al.*, 2008). From this
significance, the examination of PCDD/F formation, suppression and release from industrial combustion and manufacturing is shown to be centrally focus field of study with up to 600 journal articles being published in the past 20 years (Karstensen, 2007; Rocha et al., 2011). Comparatively, the understanding and study of other unintentionally generated POPs (such as dl-PCBs and polybrominated dibenzo(p)dioxins and furans (PBDD/F)) from cement plants are not as well documented, with Conesa et al. (2016) emphasising the difficulty in their measurements being either their lack of presence in the flue gas or the analytical ability to detect them. Not disregarding this possibility, even if a plant performs to its engineered conditions achieving stoichiometric combustion, the realistic emanation is that incomplete combustion and pollutant formations do occur. To-date, the number of journal published articles on dl-PCB and PBDD/F emissions from cement manufacturing resides at less than 100 documents (Rocha et al., 2011).

Like PCDD/F, there are 209 PCB congeners of which about 130 different individual congeners are found in commercial PCB products. Most PCBs molecules will have between 4 or 6 chlorine atoms substituted at the possible 10 sites, and are virtually insoluble in water and highly resistant to many oxidants and to degradation. This requires for all compounds to be within a biphenyl structure (i.e. 2 benzene rings linked together) which has been chlorinated as seen in Figure 2.13. Of these, there are 12 congeners which have toxicity equivalency factors assigned to them by the WHO as they exhibit dioxin-like toxicity (UNEP, 1999 and 2001). PCBs are shown to bio-accumulate in fatty tissues when exposed, with an acute exposure to high PCB levels resulting in skin rashes or burning, eye irritations, disturbances to the liver function, dizziness, memory loss, nervousness or fatigue. Chronic effects from low-levelled PCBs are shown to include liver damage, reproductive and developmental deficiencies, and carcinogenic health implications as classified by IARC (Ahlborg et al., 1994; UNEP, 1999).

2.4 Legislative Framework

So how are climate change and health-safe levels determined? The categorisation of a substance safe level is derived from its effect on the environment and its living inhabitants, based on the substance toxicity, chemical and physical properties, source, and its concentrations. In general, the licensing standards delineated by environmental protection agencies are becoming increasingly stricter. However, not all developing economies have the appropriate infrastructure or national policies in place (EA, 2005a; Karstensen, 2007), so a better understanding of the effects and impacts under varying co-
incinerating options is somewhat paramount. As most licence conditions for each situation is derived from its case-by-case evaluation, the emission limits placed on industries by the governing agency are generally more rigid than guidelines set out by the WHO and the IPCC. For legal implications, information regarding site-specific emission limitations on the combustion processes in the Appendices will not be available for this study. However, as a guideline, it can be assumed that all these processes have governing license emission limits and are aligned (if not below) international standardised values.

Legislative frameworks have been carved from detail scientific research, publications and numerous international agreements, of which Hasanbeigi et al. (2012a and 2012b) highlights the guidance of these with other hold points (e.g. quantified waste inputs, proper sorting, pre-treatment, permitting) can make waste co-incineration a more attractive alternative. The Kyoto Protocol established by the United Nations Framework Convention on Climate Change (UNFCCC) aims to internationally-bind nations to emission reduction targets. To date, the Kyoto Protocol has been subject to much industry, academic and public criticism as it struggles to balance the environmental-energy dilemma. With substantial delays, equities, economic, and capitalisation tribulations, the European Union (EU) has sequentially established several legislative measures in relation to the reduction of CO\textsubscript{2} emissions.

One of these is the European Trading Scheme (ETS), introduced in 2005, which also impacts the allowance on incentives for technological improvements and the adoption of environmentally sound management (ESM) and BMP. The economic ETS has been conceptualised for several decades and essentially allows for polluters to transfer the reduction of pollutants from other regions. However, it doesn’t resolve the displacement of criteria and hazardous pollutants from its urban neighbours. Even with forceful legislation, the localised carbon intensity from its cement industry has decreased 3-5%, however this is reported to be due to other incentives outside of the strategy. This case scenario provides concerns and doubt that an emission trading scheme enforced by superior regulating authorities will not alone defy the invasive global CO\textsubscript{2} mass emission release (Goisis, 2014; Villano, 2014). This concern is reinforced by UNEP (2014a) whereby the target 450 Scenario is not being achieved through the current volunteering program made by pledged countries. As the cement industry is a major CO\textsubscript{2} global emitter, its influencing contribution could be with the co-incineration of alternative fuels with a low CO\textsubscript{2} UMEF (Hasanbeigi et al., 2012c).
Within Europe, the European Commission (EC) initiated directives during the early nighties on the incineration of hazardous wastes (directive 94/67/EC) which required the evaluation of several POPs, specifically with the formation and release of PCDD/Fs (EC, 1994). The EC Directive established a dioxin release limit of 0.1 ng I-TEQ/Nm$^3$ for compliance over a 6 to 8-hour period as well as other regulatory limitations (e.g. minimum temperatures, maximum halogenated organic concentrations). Additional directives have also come into force through the EC (2000 and 2008) which also focused on the co-incineration of hazardous waste within cement plants and its management of emissions, specifically achieved through the adoption of the European Integrated Pollution Prevention Control Bureau (EIPPCB) Best Available Technique Reference (BATRef) documents (EIPPCB, 2006 and 2013; UNEP, 2008). From this, there is a common emission reference placed on specific pollutants when cement plants utilise the co-incineration of alternative fuels (notably directive 2000/76/EC), as shown in Table 2.4. Through decades of research and evaluation, the European legislation and its cement industry has jointly applied several solutions to achieve environmental performance in a cost competitive world (Supino et al., 2016).

Table 2.4: Regulated air emission limits for new cement plants (EC, 2000; EIPPCB, 2013; Kerton, 2014).

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Total emission limit [mg/m$^3$]</th>
<th>EC Directive 2000/76/EC &amp; BATRef limit</th>
<th>USEPA NESHAPs limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSP</td>
<td>&lt;10 (12-20 for existing plants)$^5$</td>
<td>3 (10 for existing plants)</td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>10</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>Hydrogen fluoride (HF)</td>
<td>1</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>NO$_x$ (expressed as NO$_2$)</td>
<td>200 - 450</td>
<td>325</td>
<td></td>
</tr>
<tr>
<td>SO$_2$</td>
<td>50$^6$ - 500</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>TVOC</td>
<td>10</td>
<td>27$^7$</td>
<td></td>
</tr>
<tr>
<td>Cd + Tl</td>
<td>0.05</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Hg ($\mu g$/Nm$^3$)</td>
<td>0.05</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

$^4$ Note this standard is not standardized to a reference O$_2$ or CO$_2$ percent

$^5$ Due to the effects of heavy metals (not including Hg).

$^6$ When burning waste (unless demonstrating that emissions do not arise from combustion), with the average daily concentration standardized to STP, dry and 10% O$_2$

$^7$ 21 ppmv total hydrocarbons (expressed as propane equivalent)
| Sb + As + Pb + Cr + Co + Cu + Mn + Ni + V | 0.5 | - |
| PCDD/F | 0.05 - 0.1 ng I-TEQ/Sm³ | 0.15 ng I-TEQ/Sm³ |

The added formation of Stockholm Convention agreement (UNEP, 2001) requires for the implementation of ESM on contaminated or POP-containing waste with a destruction and removal efficiency (DRE) of >99.9999 vol.% (UNEP, 2008). With a known ADF feed rate (ADFfr), this requires for the principle organic constituent destruction removal efficiency (DRE) to be calculated as (USEPA, 1987a):

\[
DRE = \left( \frac{ADF_{fr} - \text{emission rate}}{ADF_{fr}} \right) \times 100
\]

(2.7)

Furthermore, Article 2 of the Basel Convention, ESM requires for practicable steps be undertaken so that the management of hazardous wastes does not impair any human or environmental health from PCDD/F, PCBs and hexachlorobenzene (UNEP, 2012 and 2014). This requires for appropriate ESM measures with the disposal of hazardous materials and that companies involved take the necessary steps to prevent all forms of pollution (e.g. air, soil, water, noise). The United Nations Environmental Programme (UNEP) recently published its technical guidelines on the co-processing of hazardous wastes in cement kilns, which focuses on supporting the proper operations (and management) of waste materials, whilst achieving the near-complete destruction (and minimising emissions to required standards) of hazardous and POPs, (Degré, 2014; UNEP, 2011 and 2012).

Relative to the United States of America, the National Emission Standards for Hazardous Air Pollutants (NESHAPs) issued under the Federal Register regulates the emission of HAP from industries, including clinker production. Different to the EU’s cement industry co-processing regulations, which originated from concerns about waste generation, pollution, and landfill shortages, the USEPA NESHAPs limit are largely the result of concerns related to environmental protection and the implementation of the 1970 Clean Air Act. Due to its recovery of energy during co-incineration of hazardous materials, cement plant emissions are required to conform to the limits shown in Table 2.4.

Within Canada, proposals for new clean air regulations by the Environmental Registry (2014) show progress being made in the last few decades with annual CO₂ emissions reduced by 3 vol.% to 176 Mt. With Ontario’s 2020 and 2050 target CO₂ reduction
respective to 15 vol.% and 80 vol.% on historical 1990 emissions, opportunities (by fuel and material substitution) remain for further emission reductions in many other energy-intensive and trade-manufacturing sectors, one of which is cement. The application of the regulation is primarily for industries to gain approval, and take advantage of reducing coal and petroleum coke through the integration of low-carbon fuels (Environmental Registry, 2015; Pembina Institute, 2014). As defined within the regulation, these ADF have a CO₂ emission intensity less than that when coal or petroleum coke is used, and would include the use of plastics, paper materials, used tyres, hazardous waste and certain liquid wastes (Environmental Registry, 2014).

Even with these alternative fuel options being available to explore, certain fuel criteria (e.g. calorific value and maximum contaminant concentrations) are required to still be met. This does however, still permit for the flexibility to research and present additional testing potentials on other low-carbon fuels. Overall, the Ontario government believe that 5-10 vol.% of GHG emissions can be reduced through key energy-intensive industries, and further reports indicate that substantial cost savings can be achieved as well (Environmental Registry, 2015; Karstensen, 2014a). Pembina Institute (2014) reviewed the performance of existing plants, noting the best opportunity for achieving the government’s GHG reduction objective is through alternative fuel substitution.

2.5 Process Parameters which Influence Combustion

Cement plants are independently designed and can vary due to considerations on receiving materials types and customer quality expectations. The combustion and process parameters involved are somewhat integrated and influenced by each other, making subtle changes even more complex. It can be these limitations which drive the suitability of a substituting fuel and the challenges that complete combustion may have. This section reviews the combustion of solid fuel characteristics, and key parameters which influence its efficiency and transfer of energy.

2.5.1 Combustion of solid particles (i.e. effects from fuel sizing)

Combustion is fundamental to cement manufacturing design, and for large solid combustible matter (either sourced from the fuel or raw meal) it includes continuous drying, pyrolysis and oxidation (Figure 2.14). Fuel drying and pyrolysis is the chemical change of fuel to heat which involves the rearrangement of structured molecular bonds.
As suspended fuel particles are heated by gradients of gas radiation and convection, IM and volatiles are subsequently released (Alsop, 2014; Karstensen, 2007).

<table>
<thead>
<tr>
<th>Path</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Direct devolatilisation of fuel to gas</td>
</tr>
<tr>
<td>B,C</td>
<td>Formation of liquid or tar products</td>
</tr>
<tr>
<td>D</td>
<td>Evaporation of liquid or tar</td>
</tr>
<tr>
<td>E,I</td>
<td>Ongoing devolatilisation &amp; char formation</td>
</tr>
<tr>
<td>F</td>
<td>Fragmentation into smaller particles</td>
</tr>
<tr>
<td>G</td>
<td>Conversion to shrinking particle</td>
</tr>
<tr>
<td>H</td>
<td>Converted particle of a constant size &amp; shrinking core</td>
</tr>
<tr>
<td>J</td>
<td>Agglomeration to form a larger particle</td>
</tr>
<tr>
<td>K</td>
<td>Reshaping of virgin fuel particles</td>
</tr>
</tbody>
</table>

**Figure 2.14:** Typical pathways for conversion reaction of a solid fuel particle, with a particle cross-sectional view of in-situ transfers (Source: Larsen, 2007).

Where the fuel particle is of size and the external char layer is maintained during initial devolatilisation, some additional physical processes continue to occur through a reacting layer to the virgin fuel. As thermal energy is conducted into the particle layers, radiative heat forces cause further devolatilisation and an outward mass transport (Figure 2.14), leading to a slow heterogeneous conversion of char (Di Blasi, 2009; Larsen, 2007). The particle’s mass-loss rate from devolatilisation is shown by the kinetic reaction model (Commandré et al., 2005):

$$\frac{\partial m_{\text{solid}}}{\partial t} = k_{\text{dev}} \cdot m_{\text{solid}}$$  \hspace{1cm} (2.8)

$$k_{\text{dev}} = A_{\text{dev}} \cdot \exp \left( \frac{E_{\text{dev}}}{R \cdot T_p} \right)$$  \hspace{1cm} (2.9)

The initial products of devolatilisation generally include CO, CO₂, hydrocarbons (CₓHᵧ), and H₂, which may undergo additional oxidation towards stoichiometric combustion (i.e. to produce end-products of CO₂ and water). The stoichiometric equation which provides the right amounts of reactants for theoretical complete combustion is shown as:
\[ C_xH_y + (x+y/4) (O_2 + 3.76N_2) \rightarrow xCO_2 + \frac{1}{2} yH_2O + 3.76(x+y/4)N_2 \]  \hspace{1cm} (2.10)

The exothermic oxidation of fuel and air is to produce heat and energy for carbonate decomposition within the kiln and this requires similar parameters (and equal balances) to that of boilers and furnaces, namely a balance of three T’s – time, temperature, and turbulence (Karstensen, 2007). With this, the correct form and quantity of oxygen will also need to be supplied to support the completeness of combustion and irreversible destruction of any potential pollutants. Karstensen identifies the following parameters are required to achieve \( K_{gt} \) of 1,800 °C:

- a substantial residence time for the chemical reaction, and complete pyrolysis and oxidation to occur,
- a temperature high enough to ignite and char the mixture, and
- a turbulent and complete mixing of the fuel-air mixture.

While oxidation is the chemical reaction of the organic material with oxygen until no more pyrolysis can occur, it becomes completed when the inorganic material is devolatilised so that only residual non-combustible material remains as ash (Green and Perry, 2008; Sajwan \textit{et al.}, 2006). The sizing of combustion-related particles is generally found to be with the range of 0.1-20 \( \mu \text{m} \) (Bhatti, 2011). With this and a known composition of material and fuel to be used, Stefanović \textit{et al.} (2010) shows theoretical calculations that can be applied to estimate cement manufacturing’s \( \text{CO}_2 \) emission factor (EF) (Appendix 1). A problem with these theoretical calculations is that while the calcination of raw meal may be simplistic, the combustion and co-incineration of conventional and/or alternative fuels is more complex and are dependent on other influential process parameters and mechanisms.

Relevant to material and fuel combustion, several publications (Alsop, 2014; Mokrzycki and Uliasm-Bochenczyk, 2003; Kääntee \textit{et al.}, 2004) note four important components of thermodynamics and clinker chemistry, which include:

1. Fuel and meal types and feed rates (including \( \text{ADF}_r \)) which affects the fuel combustion efficiency and thermal transfer of energy;
2. Burner temperature and \( O_2 \) vol.% which oxidises the fuel to release the heat;
3. Kiln sintering and calcination zones to provide the appropriate residence time; and
4. Mass flow and equivalence ratio of combustion and recovered air which influences the thermal efficiency of the system.
For the overall cement manufacturing process, the typical evolution of the gas and material temperature profiles through the differing stages can be seen in Figure 2.15.

![Figure 2.15](image)

**Figure 2.15**: Typical gas-material temperature distribution for a PH/PC-kiln system (Source: Mokrzycki and Uliasz-Bochenczyk, 2003).

As combustion within the kiln is primary to the success of the overall process, it itself is a complex process which involves thermodynamics, fluid mechanics, chemical kinetics and transport process. For the process parameters that influence combustion within the kiln, these are generalised to include the following efficiencies.

### 2.5.2 Combustion flame temperature

The rate at which combustible compounds are oxidised, and calcination is maximised to produce quality clinker, is influenced primarily by constant and high flame temperatures within the rotary kiln ($K_f$). The heat needed to combust fuel, material calcination and pollutant restraint is greatly dependant (as seen in Figure 2.16) on the combustible concentration, kiln chamber temperature, heat loss, kiln design, and flame residence time. These parameters can further influence the stability of the $K_f$, its length and the burning zone, and the fuels’ thermal conductivity capacity in heat transfer by molecular mechanisms (Boubel et al., 1994).
With up to 95% of heat transfer occurring in the kiln by radiation, its completeness is dependent on the short residence time of the material (K_{rt}) within the burn zone length. With a high gas velocity, the value of this heat transfer is proportional exponentially to the K_{rt} and meal temperature (K_{mt}) (Young and Miller, 2011). Hansen (2003) notes the dependency on K_{rt} and its stability can further challenge ADF co-incineration so that production capacity and clinker quality is not compromised. With its inherently different composition and structure, the use of ADF can lower the flame temperature due to volatile compounds and IM content. From this, it is considered necessary that a fuels’ CV is maintained above 550 °C primarily due to its ignition and degree of decarbonation. By sustaining the momentum of the kiln burner, the stability and temperature of the flame (in either precalciner vessel or kiln chamber) can therefore be at the expense of the selected fuel and its handling conditions. As flame optics are increasingly monitored and controlled by multi-dimensional data of the flame and kiln sintering zones, the main difficulty remains to be fuel ignition temperatures, flame speed and the influence of excess O_2.

VDZ (2007) investigated the continuous plotting of numerous temperature measurements (flame, fuel, kiln chamber, combustion air, and meal) showing each of these to subsequently reduce the impact of burner operations and fuels used. Neuffer and Laney (2007) further examined this, showing the greatest effect to flame temperature was particularly notable with the ADF_{fr} and its initial temperature. As the burner uses an oxidiser (usually air/O_2) to combust the fuel and convert the chemical energy into thermal energy, its mixture can stabilise the flame temperature and achieve the desired release and distribution of heat. Recent designs now incorporate BAT on pollutant formation,
however this is sometimes not easy as pollutants are often affected by each other (i.e. inhibitors and catalysts) and emissions can be counter-generated, as seen in Figure 2.17.

![Figure 2.17: Dependence of NO and CO on equivalence ratio (Source: Baukal, 2004).](image)

2.5.3 Combustion air

Part of the combustion triangle is the presence of air or, more importantly, oxygen. For optimised co-incineration, Lauber (1982) extends that oxidation should be a dominate function, with pyrolysis being either incidental to combustion or so that it places material in a preferable form for oxidation. A fuel’s complete combustion requires a stoichiometric amount of oxygen (at a mixture equivalent ratio with fuel) to be present. If an insufficient amount of oxygen is supplied, then the system is considered rich, and alternatively if there is excess oxygen supplied, the mixture is stated as lean (Mycock et al., 1995). It is however important to note the significance and dramatic effect that O\textsubscript{e} can have specific to combustion within the kiln if not maintained, as opposed to the overall plant (more-so PH/PC tower) effects from the amount of O\textsubscript{e}. Outside of stoichiometric and efficient-mixing conditions, the adiabatic flame temperature will be lower in a lean environment (Young and Miller, 2011).

In combustion, the efficient mixing of fuel and air (both primary and secondary) in a turbulent form is significant. For complete combustion, the fuel must initial come in contact and mix with the primary-air at the flame, or must be oxidised further downstream at hotspots. Where the fuel type or meal feed rate is not constant, dead spots are created which can lead a proportion of this combustion to form particulates and gaseous pollutants (Karstensen, 2004b). This is primarily controlled through the application of the kiln induced draft fan along with fuel firing at the burner, whereby the fuel-air mixing rate assists flame stability and so that these hotspots are not created. There are, however,
process influence which can alter the oxygen at the kiln exit and therefore controlled by additional CO and O$_2$ analysers at the tertiary air vent near the precalciner (Alsop, 2014; Young and Miller, 2011).

With a burner’s momentum, the primary-air is mixed rapidly at the nozzle with good flame stability and temperature, while the surrounding secondary-air is required to be entrained around this initial fuel-air combustion jet. With the secondary-air having a high temperature, this supports flame stability and achieves a higher K$_f$. The recirculation and momentum of this secondary-air further assists the kiln to achieve its required aerodynamics and inhibitor towards pollutant formation. For tertiary air, its temperature is effective in providing an adequate flame and precalciner temperature, but this cannot be too high as it will overcompensate the PC cyclone system or initiate POP formation in the APCD. CSI (2006) evaluated plant performance with 2200 measurements of PCDD/F and PCB, showing that a reduced temperature at the APCD inlet is significant reducing factor to post-combustion catalytic formation of PCDD/F and PCBs, independent of waste type and ADF$_{fr}$. The formation patterns and amount of PCDD/F and PCBs within the selected APCD (predominately being ESPs, baghouses or a combination of both) is shown to vary greatly between PH-PC kiln systems, and therefore need to consider a combination of other process operating parameters (e.g. fuel sizing and firing rate, flame temperature, residence time).

With a strong correlation to thermal energy, an O$_2$ rich kiln can have significant influencing effects to most parameters (including fuel firing rate, secondary air temperature, flame and chamber temperature) and to the later sections of the plant PH/PC tower (including tertiary air, gas and material temperatures, flue gas emissions, and average clinker production rate). The effect of temperature loss is caused by the heating of excess oxygen and the additional nitrogen content passing through the PH/PC. This effect becomes reduced as the amount of O$_e$ decreases to a minimum (Alsop, 2014).

As shown in Figure 2.18, the reduced level of oxygen within the flame will lead to the generation of PICs, predominately being carbon monoxide (Bhatty, 2011). The influence of excess O$_2$ extends to the flame length as generated by the IDF speed, contributing to the generation of PICs and NO$_x$ as the heat responsiveness to optimal fuel-air mixing is proportionally reduced (Alsop, 2014). This in-efficiency can also have larger associated costs due to plant maintenance and fuel-energy demands. However, this general correlation of oxygen content into the kiln needs to be flexible and not set in concrete, as
it will ultimately be determined by the plant capabilities. Under a model simulation of ADF co-incineration, Kääntee et al. (2004) identified that for the use of MBM and sewage sludge, up to 3-4 vol.% more air was required to support the gasifier with large amounts of substituted fuel (ADF%).

![Figure 2.18](image)

**Figure 2.18:** Effects of oxygen level on exit gas heat loss (Source: Alsop, 2014).

For clinker production (including PH/PC tower), the amount of air used is predominantly leaner than theoretical amounts as most devices are not capable of achieving ideal mixing. The amount of O$_2$ needs to be minimal to reduce heat loss from the system and additional fuel is required so to burn off the excess O$_2$. According to Worrell et al. (2008), the infiltration of unnecessary air can result in heat loss equal to 75 MJ per tonne (MJ/tonne) of clinker. Hesketh (1994) formulated an Orast validation graph (**Figure 2.19**) giving a correlation on the stoichiometric amount of oxygen required for systems utilising various forms of fuel, and thus extrapolating the amount of O$_2$ needed for complete combustion.

![Figure 2.19](image)

**Figure 2.19:** Orast validation nomegraph (Source: Hesketh, 1994).

Additionally, the continuous monitoring of CO, NO$_x$ and O$_2$ within the flue gas provides an indication on the amount of O$_e$ within the process. With lean levels of air, it is shown that NO$_x$ UMEF will increase as the flame temperature increases. As the effects of an
energy efficient plant (and net product produced per unit of energy) can determine its success, the control of the combustion zone temperature to a minimum optimum functionality is largely dependent on the control of its O\textsubscript{e} levels (Neuffer and Laney, 2007).

As a stoichiometric amount of oxygen is required for combustion, an O\textsubscript{2}-enriched kiln chamber will subsequently alter the flame length and temperature, burning zone, material temperature, and combustibility of low volatile fuels or waste materials (e.g. petcoke, RDF, tyres) (Bhatty, 2011). Under these conditions, a higher flame temperature will aid the reduction of NO\textsubscript{x} formation due to increased N\textsubscript{2}, however this will consequentially alter the fuel firing rate (K\textsubscript{f}), combustion and sintering zones, and the material’s temperature phases (as seen in Figure 2.5). These alterations are shown to alter clinker quality due to potential over-burning. The innovation of O\textsubscript{2}-enriched kilns has gather attention over the past decade, with a technological basis of replacing combustion air with a mixture of near-pure O\textsubscript{2} (> 90 vol.%) and recycled CO\textsubscript{2} flue gas from the kiln (Ariyaratne et al., 2013a). Zeman and Lackner (2008) show the use of this can result in a greater CO\textsubscript{2} UMEF under normal operating conditions, controlled by its later capture and storage. While this is shown to be an effective method towards reducing category pollutants such as acid gases (e.g. NO\textsubscript{x}, SO\textsubscript{x}) and particulates, it remains to still rely heavily on other downstream technologies to achieve CO\textsubscript{2} objectives set by the target 450 Scenario.

2.5.4 Residence time

As high temperatures are used throughout cement manufacturing, a short residence time in the can also achieve the same degree of fuel oxidation and material calcination. Alternatively, complete combustion with lower temperatures (and less fuel and maintenance) can be accomplished by increasing the residence time, although this in-turn can influence the generation of combustible and non-combustion pollutants. To optimise devolatilisation and stoichiometric combustion, the K\textsubscript{stt} is a significant process parameter needing to be held constant, so there is a fine balance on increasing the residence time too much (Green and Perry, 2008).
2.5.5 Fuel firing rate and fuel-air ratio

2.5.5.1 Fuel firing rate

The efficiency of fuel combustion (and its subsequent feed rate) is related to several important physical characteristics, namely the substance specific heat, thermal conductivity, specific mass, flammability limit, CV, flash point, and viscosity. Greco et al. (2011) identify that, even though all process inputs must be controlled, the mass flow of fuel is particularly critical. With a surge or lapse in the fuel firing rate, temperature drops and non-stoichiometric conditions will occur, effectively altering the fuels’ thermal conductivity and potential for complete combustion. This can also alter the kiln burning zone, whereby an increase will lengthen the zone length and exposure the product to high temperature longer, or a decrease will shorten the zone length and affect the clinker quality. A process counter-balance to this is to increase or decrease the kiln revolution speed, though this is not preferred due to upstream precalciner and preheater disturbances.

The fuel CV is not typically influenced by process operations, though the fuel composition and firing rate should be constant so to maintain high combustion efficiencies. The amount of energy released per unit mass of fuel (expressed with lower heating value (LHV) and higher heating value (HHV)) can, however, become problematic and unstable if differing fuel types or states are used simultaneously (Greco et al., 2011). A report by Koppejan and Zeevalkink (2002) evaluated the material and energy potential to a fuel’s CV, showing that subsequent considerations need to consider its IM content, any fuel preheating and the amount of ash produced from co-incineration.

The chemical characteristics of a fuel is also significant to its firing rate and subsequent CV and combustion efficiencies, adiabatic flame and gas temperature, and the catalytic, formation, suppression and release of air pollutants. This is particularly important, and somewhat complicated, when the fuel composition has multiple constituents and low volatility. Therefore, the selection of a fuel and its use needs to be strategic and balanced so to meet the operational, socio-environmental and economic conditions. Fuel characteristics of importance include the content of sulfur, IM, nitrogen and any other catalyst-containing compounds (e.g. hydrocarbon, polyvinyl chloride (PVC), sodium chloride) which can influence pollutant-forming mechanisms (as discussed in subchapter 2.6).
2.5.5.2 **Fuel-air equivalence ratio**

As cement kilns provide sufficient temperatures, residence time, turbulence and O\textsubscript{2} content, another important parameter of combustion is the mixture equivalence ratio ($S_1$) of oxidiser to fuel. From a chemical reaction, the stoichiometry formulation calculated by equation 2.11 is required to sufficiently sustain the combustion chamber with a well-mixed ratio of fuel and air (Tsuji *et al*., 2003), as seen in **Figure 2.20**. Where an improper ratio (or its uniform mixing) is not provided to the burner flame, incomplete combustion can possibly result in the further formation of POPs (Sidhu *et al*., 2001).

![Figure 2.20](image_url)

**Figure 2.20:** Flammable domain expressed by fuel CV, initial temperature of mixture, and mixture equivalence ratio ($S_1$) (Source: Tsuji *et al*., 2003).

Baukal (2000) identifies the equivalence ratio as an important consideration to combustion due to possible variances in the oxidiser’s inert composition and the amount required. This ratio can signify the reaction stoichiometry, as calculated by:

$$S_1 = \frac{\text{Volume flow rate of O}_2 \text{ in the oxidiser}}{\text{Volume flow rate of fuel}}$$ \hspace{1cm} (2.11)

Fuel-rich combustion conditions are achieved within the kiln when $S_1$ has a $<1.0$ ratio, whereas a fuel-lean combustion condition is achieved with a $S_1 > 1.0$ value. As the acquisition of a proper fuel-air mixture is a timely step during combustion, it is also considerably important as it can eliminate the need for additional control measures. Fuel-air mixing at the primary burner is a function of its $K_{fr}$, velocity and kiln circulation (Karstensen, 2008a).

Friction to the mixing of fuel-air can occur due to varying supply rates or the effects of the surrounding chamber (e.g. kiln wall proximity, precalciner perpendicular flow of
meal). This friction will result in the recirculation of downstream combustion gases which have a substantial effect to $S_1$, flame impingement and complete combustion. To mitigate such effects, the use of BMP can include a reduced mass flow rate of the oxidiser ($Air_i$) while maintaining the flame length and required $S_1$ where possible (Colls, 2002). More recent burner designs have included smaller oxidiser nozzles and the flexibility to alter the direction of flow.

### 2.5.6 Heat transfer

As initial heating and evaporation of IM occurs at 100 °C, the rate of these ultimately depend on the fuel particle size and composition. For small particles (<100 µm) the rate is constant, however larger solid particles will have numerous temperature gradients which will need to undergo a certain pathway (Nørskov, 2012). Green and Perry (2008) show one-dimensional heat transient equations which signify the key combustion-influencing parameters as:

1. Dimensionless temperature ($\theta / \theta_i$)

$$\theta / \theta_i = \frac{(T_{(\epsilon,t)} - T_\infty)}{(T_i - T_\infty)} \quad (2.12)$$

where $T_{(\epsilon,t)}$ is the raw meal temperature;

$T_i$ is the initial meal temperature; and

$T_\infty$ is the gas temperature.

2. Heat loss fraction ($Q / Q_i$)

$$Q / Q_i = \frac{Q}{[\rho * c * V * (T_i - T_\infty)]} \quad (2.13)$$

where $Q$ is the rate of heat transfer;

$\rho$ is fluid density; and

$V$ is volume.

3. Radius distance from the solid particle centre

4. Dimensionless time, or Fourier number ($F_o$)

$$F_o = \frac{\alpha * rt}{R^2} \quad (2.14)$$

where $\alpha$ is the thermal diffusivity;

$rt$ is residence time; and

$R$ is rate of thermal energy storage.
5. Biot number (Bi) indicates the relationship of thermal heat transfer to the particle to the internal heat transfer within the particle (Nielsen, 2012), and is defined as:

\[
Bi = \frac{h \cdot d_p}{2 \cdot \lambda_p}
\]

(2.15)

where \(h\) is the external heat transfer coefficient of fuel particle, 
\(d_p\) is the particle diameter, and 
\(\lambda_p\) is the particle thermal conductivity.

When the Biot number is small (\(Bi < 0.2\)) the solid fuel particle temperature is consistent and isothermal with the combustion efficiency being considerably high. Whereas if Biot number is higher (\(Bi > 0.2\)) then the particle is more complex and non-uniform internal temperature gradients may exist (Green and Perry, 2008; Nørskov, 2012).

2.5.7 Rate of meal feed and clinker production

Achieving optimal kiln conditions are significantly influenced if the meal feed rate is not maintained and consistent through a metering station. The provision is important to provide the kiln and precalciner combustion chambers enough quality product that absorbs the required amount of heat produced. Thermal performance modelling by Rasul et al. (2005) showed the mass flow of a typical PH/PC-kiln which is influenced 31.3 wt.% by the meal feed rate to produce a 17.9 wt.% clinker product, with significant impacts to maximising its productivity being from the rate of air (59 vol.%) and the fuel firing rate (9.7 wt.%).

2.6 Mechanisms of Pollutant Formation in cement plants

The chemistry and physics of combustion (e.g. destroying and rearranging of certain molecules) to rapidly release substantial amounts of energy from a fuel is dependent on the PH/PC-kiln components and operation. Under certain conditions, the rearranging shall give preference to one substance (e.g. PCBs) over another (e.g. PAHs) given the presence or absence of certain compounds or parameters (e.g. HCl, or temperature). To investigate and devise cost-effective improvements that may reduce contaminants from combustion, it is equally important identify and understand the source and mechanisms of these pollutants.
2.6.1 Gaseous pollutants

The main origin of CO$_2$ formation during manufacturing is from the calcination of CaCO$_3$ (at about 55 wt.%) or base-fuel combustion (at about 35 wt.%), as seen in equations 2.1 and 2.10. Its formation is a significant 30% reduction when compared to 30 years ago, although this is primarily through the advancement and efficiency of PH/PC-kiln designs. There are, however, 4 influencing parameters which primarily impact the formation of combustion CO$_2$ including (1) fuel composition and temperature, (2) oxidiser composition and temperature, (3) fuel-air equivalence ratio, and (4) gas temperature (Karstensen, 2007). Under stoichiometric conditions, CO$_2$ is also produced when the oxidisation of coal or hydrocarbon fuel is proportional to the carbon-hydrogen composition ratio shown in equation 2.10.

The influence of preheated fuel temperature (Figure 2.21a) and oxidiser composition can decrease the formation of CO$_2$ because of dissociation, however NO content is shown to slightly increase. Baukal (2004) has shown that under similar conditions and temperature the influence of fuel moisture will increase the formation of CO$_2$ three-fold over a moisture-absent system. Figure 2.21b show an increase in the oxidiser temperature (wet or dry basis) significantly decreases the formation of CO$_2$ due to dissociation, giving preference to PICs.

![Figure 2.21: Adiabatic CO$_2$ equil with preheat temperatures for (a) fuel and (b) oxidiser](Source: Baukal, 2004).

As the fuel-air equivalence ratio becomes richer ($S_1 > 1$) the formation of carbon dioxide decreases due to the lack of sufficient oxygen to combust the fuel carbon, and tends to increase the proportion of carbon monoxide and NO$_x$. In lean mixture ratios ($S_1 < 1$), the excess oxygen and lesser nitrogen also lowers the formation of CO$_2$, as seen in Figure
2.22a. The increase of exhaust gas temperatures above 1300 °C not only influence the systems thermal efficiency, but also inhibit the formation of CO₂ by dissociation, as seen in Figure 2.22b.

The application of higher thermal efficiency of waste heat recovery is a measurable control that suppresses CO₂ emission. Consequently, the temperature rise in combustion air can influence the formation mechanisms of NOₓ due to a higher flame temperature, thus exponentially increasing NOₓ formation (Tsuji et al., 2003).

![Figure 2.22: CO₂ formation as a function of (a) exhaust temperature and (b) equivalence ratio (Source: Baukal, 2004).](image)

Where incomplete combustion occurs, key by-products include CO and trace unburned hydrocarbons. Carbon monoxide is generally produced as some degree of incomplete combustion will occur, either due to poor fuel-air mixing, insufficient oxygen, high temperature for a CO₂ reaction, or gas residence time. As PH/PC-kiln systems generally run with Oₑ ensuring to reach complete combustion and therefore minimise CO, the injection pattern of fuel-air creates distributions of low oxygen regions allowing the forming of CO. A general acceptance of a near-stoichiometric conditions being achieved can permit for a low 50 ppmv CO emissions to be released (Alsop, 2014). However, when CO emissions are greatly reduced, NOₓ emissions are subsequently increased.

During clinker production, the formation and destruction processes of NOₓ are considerably complex and influenced by temperature and S₁. Two key formation mechanisms are from thermal NOₓ and fuel NOₓ, whereby the main reactions of combustion (e.g. devolatilisation, and char and volatile matter (VM) oxidation) are influenced by the inevitable PH/PC-kiln design and operation of several fuel and process parameters (Alsop, 2014; Neuffer and Laney, 2007) to produce NO, NO₂ or nitrogen (N₂).
(Cao et al., 2010; Karstensen, 2007). Thermal (or Zeldovich) NO$_x$ is formed by very high temperature reactions (>2,000 °C) of atmospheric nitrogen and oxygen, given as:

$$N_2 + O_2 \rightarrow NO, NO_2 \quad (2.16)$$

Thermal NO$_x$ increases exponentially with peak flame temperature (generally more than 1,300 °C), residence time within high temperature, air pre-heating or in-flame O$_2$ enrichment. The formation of thermal NO$_x$ is a function of stoichiometric conditions, whereby the combustion zone temperature is dependent on $S_1$. The composition of the oxidiser can increase the NO$_x$ concentration by increasing the amount of O$_2$, which increases the flame temperature and hence the generation of thermal NO$_x$. Whereas a lower flame temperature is caused due to a reduced atmosphere (i.e. low O$_2$ content), however CO is formed preferentially to NO (Karstensen, 2007).

As fundamental to combustion, the formation of thermal NO$_x$ is also dependant on the residence time of a fuel type within its optimal temperature range. Where longer residence times are experience in high temperature combustion zones with available oxygen (due to the dependency on excess O$_2$), the formation of thermal NO$_x$ is increased (Neuffer and Laney, 2007). The influencing effects of thermal NO$_x$ generated from the rotatory kiln is of significance to the overall manufacturing process, as a high concentration of NO$_x$ in the gas composition will influence the physical and chemical reactions that occur within the precalciner (Zhang et al., 2011). As the PH/PC tower utilises tertiary air from pyro-processed flue gas, its design with secondary firing has a reduced stoichiometric flame temperature (<1,200 °C) due to its O$_2$ content, effectively reducing the nearby formation of thermal NO$_x$. Therefore, allowing PH/PC-kiln systems to utilise 60 wt.% of total fuel to be combusted in the precalciner without compromising total NO$_x$ emissions (Karstensen, 2007; Tsuji et al., 2003).

The addition of a fuel-rich condition decreases NO concentrations, but can potentially increase CO. Alternatively, if fuel conditions are lean, NO increases and CO decreases. As most secondary fuels (particularly solids and liquids) and raw meal naturally contain some nitrogen, its composition may influence NO formation within the kiln or PH tower, and can be accounted for 15–100 vol.% of total NO$_x$ emission (depending on flame temperature profile and O$_2$). Where additional hydrogen or CO is present and exposed to this fuel in the combustion chamber, the amount of NO$_x$ is increased. Whereas
combustion air that contain traces of CO₂, N₂ or H₂O can decrease the generation of fuel NOₓ, on a volumetric basis (Baukal, 2004; Neuffer and Laney, 2007).

If the kiln temperature is not maintained, the formation reactions of clinker material will stop, further reducing the overall PH/PC-kiln gas temperatures. Sustaining this problem generally requires the additional rapid firing of fuel, which results in additional fuel NOₓ being formed. The overall reaction of fuel NOₓ in the system can generally be:

\[ R_xN + O_2 \rightarrow \text{NO, NO}_2, \text{CO}_2, \text{H}_2\text{O}, \text{traces} \quad (2.17) \]

Prompt (or Fenimore) NOₓ is a fast reacting mechanism between N₂, O₂, and hydrocarbon radicals, and tend to be the intermediate species formed within lower temperature regions when gas or oil fuels are utilised. The formation of prompt NOₓ is:

\[ \text{CH}_4 + N_2 + O_2 \rightarrow \text{NO, NO}_2, \text{CO}_2, \text{H}_2\text{O}, \text{traces} \quad (2.18) \]

Sulfur is also an organic element in certain carbon-based fuels (e.g. oil, coal) which undergoes oxidation during combustion, formed into SO, SO₂, SO₃, H₂S and SO₄ (Cao et al., 2010). The more common oxides (SO₂ and SO₃) are of interest as they may inhibit the formation of fuel NOₓ during combustion (Dullen, 1989), escape with the flue gas and later react with water vapour to form sulfuric acid mist. The initial oxidisation of sulfur to SO₂ (equation 2.19) occurs at combustion, with the further oxidation to SO₃ occurring between 1.25-2.5 vol.% (equation 2.20). At high temperatures, the formation of SO₂ dominates the flue gas SOₓ, and lower temperatures the formation of SO₃ significantly declines (Baukal, 2004).

Furthermore, as sulfides and organic sulfur also naturally occurs in raw meal (e.g. limestone, clay), it becomes oxidised to SO₂ within a moderate preheater gas temperature (PHₙ) of 400-600 °C with about 30 vol.% of it then being transferred to the gas phase. Where areas of moderate temperatures and oxygen concentrations exist (i.e. kiln sintering zone), further oxidisation to SO₃ can occur, however most SOₓ emissions from PH/PC-kilns will be in the form of SO₂ (Karstensen, 2007; Young and Miller, 2011), as seen in the following equations:

\[ S + O_2 \rightarrow \text{SO}_2 \quad (2.19) \]
\[ \text{SO}_2 + \frac{1}{2} O_2 \rightarrow \text{SO}_3 \quad (2.20) \]
An increase in SO$_3$ can have a subsequent effect to the clinker (decreased C$_3$S and an increased C$_2$S). With a high lime concentrate, the concentration of SO$_3$ is reduced (equations 2.21 and 2.22) due to the formation of calcium sulphite (CaSO$_3$) (Baukal, 2004).

\[
SO_2 + CaO \rightarrow CaSO_3 \quad (2.21)
\]

\[
CaSO_3 + \frac{1}{2} O_2 \rightarrow CaSO_4 \quad (2.22)
\]

TVOCs (aliphatic and aromatic hydrocarbons) are solids or liquids that vaporise quickly, and contain carbon bonded hydrogen, nitrogen, or sulfur. The formation and release of TVOCs are of considerable concern due to in-system precursor contributions to inorganic pollutants (such as PAHs, PCDD/Fs) and their out-system formation with atmospheric ozone (Colls, 2002). The formation of TVOCs during cement production is generally the result of a fuel’s organic matter (<1 vol.%) being volatilised upstream within the moderate PH$_{gt}$. This is beneficiary to the predominate process mechanisms downstream (particularly at the cooling stage), whereby the rapid and turbulent mixing of lean and rich fuel-air permits small volumes of unburned fuel to be convert into organic compounds and PICs, and therefore be retained within the tertiary combustion air. (Baukal, 2004; Karstensen, 2007). Whereas, when organic material is supplied as secondary fuel, it is destroyed due to high gas-material temperature and gas residence time (PC$_{rt}$) in the precalciner.

### 2.6.2 Particulate and trace species

Particulates of interest are the dry, fine solid particles where the chemical composition can be broad and initial presence is exerted from the source of fuel. Particle entrainment is usually the result of material passing through the combustor in high gas velocities or a subsidiary component of the fuel (e.g. metals) not being burnt off. The second formation of particulates can be through combustion-generation by the following mechanisms:

1. the vaporisation of some fuel-material components which later condense,
2. the frequent and unstable formation of molecular clusters from reactions,
3. the production of soot from incomplete combustion of solid, liquid, or gaseous hydrocarbon-rich fuels.

The formation of soot is elevated in fuels of a larger carbon ratio, may be within the flame where heat transfer is enhanced, or due to poor fuel-air mixing. The influence of
particulates on flue gas (and downstream APCDs) is largely significant as it has a
detriment impact on the formation, adoption, transport of gaseous-phase pollutants (such
as metals, dioxins, PCBs, SO₂) and is generally examined for the chemical contribution.

Hydrogen halide and halogen salts are formed when one halogen atom binds with another
less electronegative halogen or with hydrogen (from water vapour). The presence of
chlorine can have significant implications to plant performance (being a build-up on
chamber surfaces or corrosion) and the generation of POPs (e.g. PCDD/F, PCB) (Murray
and Price, 2008). The formation kinetics of hydrogen halides (in particular HCl) is greatly
dependent on the combustion at high temperatures. At low temperatures, the bulk of
chlorine remains bounded into solid chlorine of the alkali metal.

Trace metals exist (as inorganic materials or metal chelates) in virtually all forms of
fossilised fuels and behave in a variety of ways during combustion, and depend on the:

1. presence / absence of specific oxidising reactants (e.g. chlorine),
2. various combustor conditions and temperature,
3. combustion-air temperature, and
4. stoichiometric ratio.

As the fuel heats, metals begin to volatise at various independent temperatures, and
combine with other reactants including oxygen, chlorine, alkali metals, and heteroatoms
(e.g. sulfur, nitrogen). These trace elements remain in as gaseous pollutants and can exit
combustion without burning, and remain as gaseous pollutants. Some volatile metals
undergo homogeneous condensation on the surface of sticky fly-ash or bottom-ash
particles (Tillman, 1994). Previous emissions monitoring of heavy metals during ADF
substitution have highlighted its presence in flue gas is a major hazard (Conesa et al.,
2008; Giannopoulos et al., 2007b), with classifications predominately include:

1. Class I: Cd, Hg, thallium;
2. Class II: As, cobalt, Ni, selenium, tellurium; and
3. Class III: Pb, Cr³⁺, Cr⁶⁺, Cu, platinum, vanadium, tin, palladium, Sb, Mn.

Although arsenic is normally a trace concentration in raw material or combustion fuels,
it rapidly oxidises at low PHₑ and typically condenses into CKD particles. Yan et al.
(2015) performed a mass balance experiment of As within 4 separate cement plants,
showing it predominately being from the raw meal and mostly being contained in the
clinker product. The presence of Cd is shown to react with combustion gas to form halides
and sulfates, both of which are shown to vaporise at high temperatures. However, Bhatty (2011) reports the presence of chloride in the kiln can proportionally decrease the concentration of Cd. As a constituent to raw materials, the oxidisation of copper (Cu) can decrease kiln temperatures and acts as a catalyst to the adverse clinker formation of C₃S and C₂S, resulting in a heavy concentration to CKD (Bhatty et al., 2004). Also, as a trace element in raw materials (particularly clay) and fuels (coal, oils, or tyre derived fuel (TDF)), lead is a volatile compound which will mainly vaporise in the high kiln temperatures, and is either collected within the clinker product or CKD, or emitted through the flue gas.

Bhatty (2011) reports of Hg being predominately found in carbonaceous fuels (mainly petcoke or heavy oil) or waste fuels (e.g. TDF), and vaporises at modest temperatures (between 200 - 700 °C) into the kiln gas and partially entrained within PH particulates (Mlakar et al., 2010). A mass balance study by Yan et al. (2015) supports this by showing most Hg is from the combustion fuel (i.e. lignite) rather than raw meal (e.g. Hg being mainly from ash), with up to 77 vol.% released in the flue gas and not contained as much within the clinker product or APCD. Similar to Hg, nickel is reported (Bhatty, 2011) as a trace element in fuels (coal, oil, petcoke) as well as raw materials (limestone, clay, shale), with it being non-volatile and predominately incorporated at the clinker C₃S phase or within the CKD.

Correlating the mass-balance of metal compounds within a PH/PC-kiln, both Guo and Eckert (1996) and Eckert et al. (1999) examined the speciation and distribution of certain metals (As, Be, Cd, total Cr, Pb) amongst the 3 output streams: cement clinker, CKD and stack emissions. The calculations, however, are performed with basic analysis of CKD and stack compositions, with the remaining mass balance being assigned to clinker product rather than its analysis. Eckert et al. (1999) prescribe these limitations are due to theoretical predictions being exceedingly complex and subjected to numerous variables (namely sample representation, analysing low metal concentrations, sampling of gaseous metalloids).

From data subsets collected from 5 differing kilns, Guo and Eckert (1996) report the distribution coefficients to be consistent amongst 4 compounds (As, Be, Cd and particularly Pb), with the more volatile compounds Cd and Pb being more sensitive to CKD recirculation than other process parameters (e.g. temperature, residence time). These semi-volatile metals are conclusively able to escape within the flue gas as either
gaseous, fine particulates, or attached to PM. Eckert et al. (1999) conducted similar investigative works from data collected from 6 other kilns, concluding with identical results and conclusions. Aside from these compounds, many other metal and metalloid substances (including As, Be and total Cr) are slowly oxidised, refractory and encompassed within clinker product (Bhatty, 2011; Guo and Eckert 1996).

2.6.3 **Inorganic compounds**

Inorganic PAHs are formed during incomplete combustion whereby after pyrolysis and oxidation, fatty acids undergo cyclization and aromatization to form alkylated benzene and naphthalene from aliphatic precursors. The complete and incomplete combustion of carbonaceous material permits the free radical formation of complex PAH molecules in chemically reducing atmospheres with high temperatures (> 700 °C) (Sidhu et al., 2001). Independent of combustion fuel types, the formation of dioxins in cement plants has been greatly studied in more recent years (Altarawneh et al., 2009; Karstensen, 2014b; Li et al., 2016; Thuong et al., 2014; Zemba et al., 2011) due to the inherent ability and presence in varying anthropogenic sources such as coal or wood combustion, paper and pulp milling, waste incineration or chemical manufacturing. Relative to cement kilns, it alone is a significant contributor (> 10 wt.% of PCDD/F) in the environment, which is seen to be one of the most contentious chemicals (Chen et al., 2016).

The formation of PCDD/F involve extremely complex and heterogeneous chemical reactions which are largely dependent on process variables and conditions (Huang and Buekens, 1995). As research continued to investigate, a more-defined understanding of the mechanisms which support its PCDD/F formation has developed as well as the design and operational attributes which control its release (Abad et al., 2004; Huang and Buekens, 1995; Stieglitz et al., 1989; UNEP, 2008; Vogg and Stieglitz, 1986; Xhouuet et al., 2001). Several studies (Conesa et al., 2008; Giannopoulos et al., 2007; Karstensen, 2008a) suggest the formation and release of PCDD/F is an inevitable and integrates component to cement manufacturing.

Nevertheless, two key mechanisms remain to the formation of PCDD/F as either homogenous (gas-phase only between 500-800 °C) or heterogeneous (gas-solid interaction at 200-400 °C) (Karstensen, 2007). Studies by Wehrmeier et al. (1998) and Sidhu et al. (2001) support this and other PCDD/F literature of congener thermodynamic formation and stability, particularly with being reliant on the fuel’s composition and
influence by their respective reactivity and maxima abundance as the gas passes through the preheating and cleaning zones where temperatures reach a 250-400 °C window (Figure 2.23). Vogg and Stieglitz (1986) also signify favourable formation conditions of PCDD/F congeners under heterogeneous conditions, with concentrations being 5-fold at low temperatures of 200-300 °C (generally within the post-combustion cooler region), formation rate being its highest at about 400 °C, and with a significant destruction in its presence proportional to increased temperatures of 400, 500 and 600 °C.

![Figure 2.23: Dualistic principle of PCDD/F formation and destruction (Source: Wehrmeier et al., 1998).](image)

Thus, dioxin formation by gas-particle interface in clinker production is predominately through the De Novo (most likely) or precursor mechanisms. The first dioxin-forming mechanism is chemically different whereby dioxin formation is from organic carbon particulates being chlorinated on the surface by De Novo Synthesis, and undergo further reactions. A build-up of these compounds can form kiln rings or blockages within the PH/PC tower, however the majority of these will be encompassed with the incoming flow of meal feed at the calcination zone (Bhatty, 2011). This phenomenon involves heterogeneous, surface-catalysed reactions between the particulate and an organic/inorganic chlorine donor (Stieglitz et al., 1989; Vogg and Stieglitz, 1986) either because of:

- poorly-mixed combustion from simultaneously fuel-lean and fuel-rich conditions (Babushok and Tsang 2003; Chen et al., 2014), or
- the vaporisation and cyclic formation of alkali chlorides from the raw material composite containing chlorine (e.g. as sodium chloride or potassium chloride from
limestone, clay or shale) which later condense outside the high-temperature sintering zone (Bhatti, 2011; Oerter and Schneider, 2010).

The second dioxin-forming mechanism is by heterogeneous reactions which involve unburnt gaseous carbon to combine with chlorine donor (in the presence of a catalyst, such as Cu, Fe or other metal) to form a precursor compound (e.g. chlorinated benzenes, phenol, or biphenyls). This compound later condenses with a solid particulate in temperatures of 250-400 °C, to form aromatics and aliphatics (Baukal, 2004; Sidhu et al., 1994). The formation of PCDD/F through either of the two mechanisms is simplified in Figure 2.24, and can generally be assessed as to which mechanism is dominant through the PCDD/F ratio (De Nevo synthesis < 1 > precursor).

Figure 2.24: Formation of dioxin-like compounds (Source: Baukal, 2004).

Subsequent studies show the formation of PCDD/F formation is greatly controlled by reducing flue gas temperatures to <260 °C and not necessarily the combustion fuel composition (El-Kabbanya et al., 2015). Aranda-Usón et al. (2013) support this argument by adding the composition of conventional fuels rarely support dioxin formation, whereas some alternative fuels can contain favourable precursor or catalytic compounds, particularly MBM, sewage sludge, general waste, and wood-containing materials. The formation of furans is more predominate with reactions on fly ash surfaces in high temperatures (≈700 °C), however the breakdown of pre-existing PCDD/Fs will occur at temperatures above 790 °C (Giannopoulos et al., 2007b; Young and Miller, 2011).
In summary, the key mechanisms which promote PCDD/F formation includes:

1. gas temperature window of 200-450°C exists;
2. unburnt carbon and/or organic carbon particulates is available;
3. oxygen and chlorine is available;
4. a surface exists (e.g. particulate, equipment) to support the catalytic reaction; and
5. a catalyst (e.g. Cu, Fe) is available, and
6. sufficient reaction time within the chamber is available.

Rivera-Austrui et al. (2012) investigated long-term continuous sampling of PCDD/F, showing a comparative emission of 0.0016 ng I-TEQ/Nm³ (with petroleum coke) against 0.009 ng I-TEQ/Nm³ (substituted with tyres, sludge, wood). Within all sample tests, congeners 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF were identified with the greatest concentrations (partly due to their higher I-TEQ values).

Similar to PCDD/Fs, experimental studies of PCBs have shown them to be a subset of synthetic organic chemicals, and due to their thermal and chemical stability they have been produced for its use as electric fluids in transformers, in heat transfer and hydraulic systems, in plastic manufacturing, within lubricating and cutting oils, and as a plasticizer within paints, surface coatings and rubber seals (UNEP, 1999). Controversy, Genon and Brizio (2008) identify that even though most PCDD/F concentrations are shown to be below the EC Directive concentration of 0.1 ng I-TEQ/Nm³, problems can arise during the co-incineration of some ADFs subsequently emitting PCBs 1,000 times higher than allow concentrations. This is particularly evident where the $K_{gt}$ and $K_{rt}$ support the volatilisation of chloro-aromatic compounds.

### 2.7 Control of Air Pollutants

It is evident the initial motivation for clean air is the protection of human health, however, recent developments of environmental awareness and global greenhouse changes has delivered more specific attention to the capture of combustion pollution. It is possible to reduce man-made emissions into the atmosphere by good control procedures (Baier, 2006; Clauzade, 2006: Hesketh, 1994). Three general methods prosper good quality air, including good complete combustion, variables that inhibit pollutant formation, and the application of post-combustion control technologies. The first 2 of these methods have been discussed within subchapter 2.5 and 2.6.
Relative to post-combustion control devices, significant improvements have occurred over the past few decades, with the focus of reducing PM to an acceptable limit. As cement manufacturing produces PM from various particle-forming mechanisms, the aerodynamic diameter and shaping of these are largely dependent on physical attrition, mechanical dispersion, combustion burnout, condensation, calcification, chemical reactions and evaporation (Bapat, 2001; Richards and Martin, 2011).

With these multiple mechanisms occurring throughout the PH/PC-kiln, the sizing of PM produced can range from large to fine particles, with the latter being defined as ≤3 µm due to the increased difficulty in controlling emissions of these particles. For the purification of PM (either in wet or dry methods), the primary mechanisms in which the particle touches the target (liquid, fibre, media etc.) are impaction, interception or diffusion as seen in Figure 2.25. The selection of APCD will greatly depend on the characteristics of the PM and its carrying gas.

**Figure 2.25:** Particle-interface mechanisms by (a) impaction, (b) interception, (c) diffusion (Source: Schnelle and Brown, 2002).

At present, APCDs are maintained to acceptable levels by ESPs\(^8\), filtration with baghouses\(^8\), gravity settling chambers\(^8\), cyclones\(^8\), activated-carbon absorption\(^9\), and/or scrubbers\(^8,9\) (Hesketh, 1994). For the cement manufacturing industry, the removal of pollutants from the flue gas is predominately the first two technologies (sometimes as a combination), with the occasional plant using wet scrubbing. The selection and capacity of these units is largely proportional to the intensity and temperature of the effluent, and the regulatory release limits (Bapat, 2001; Karstensen, 2007; Karstensen et al., 2016).

ESP\(^s\) remove particulate matter by charging the particulate by corona discharge leaving the electrodes (ionization), driven towards oppositely-charged collecting plates by electromagnetic forces, and finally remove accumulated particles from the plates for

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\(^8\) For removal of particulate pollutants
\(^9\) For removal of gaseous pollutants
disposal. ESPs are most popular within the cement industry due to the high efficiencies (95-99 wt.%) for small (< 1 µm) and coarse particulates, handling very large gas volumes with low pressure drop, and can be designed for high flue gas temperatures ranges. With carbon monoxide becoming present in the gas stream through incomplete combustion and later oxidation, its levels within ESPs need to be controlled so that its concentration remains below an explosion limit (Richards and Martin, 2011).

Fabric filter collectors (referred to as baghouses) remove small particles from the gas stream by interception (colliding and attaching) onto a fibrous or porous filtering media, generally referred to as bags. Tubular bags about 30 cm diameter are attached to a metallic tube sheet located above the hopper, and are filled with unconditioned gas from an inlet. To prevent an excessive pressure drop with particulates accumulating within the bag, mechanisms (bag swinging, shakers, reverse-air or pulse pressure) are used to disengage the collected particulate from the filter (Karstensen, 2007; Schnelle and Brown, 2002). Techniques for bag cleaning may vary as they are dependent on the characteristics of the dust particles and the fabric material.

The use of baghouses provides a high collection efficiency of coarse and submicron particulates (up to 99.95 vol.%), however it can face process challenges and efficiencies with flue gas fluctuations, pressure drop (ΔP) and dust loadings. As depositing particle sizes on the filter structure decrease, it increases the resistance to the air flowing through it, creating a pressure drop. Fluctuations are further created as bags are cleaned and the gas flow continues to vary (Hinds, 1999). The successful design and use of the baghouses is key to certain design parameters; including bag material, fabric cleaning method, air-cloth ratio, air flow, and static ΔP guages (Wang et al., 2004).

Wet scrubbers work on the principles of absorption where a material from a gas is diffused through a gas-liquid interface, and ultimately dispersion into the liquid. The means are provided to break the liquid up into small droplets of thin films with high liquid surface area for mass transfer (Cooper and Alley, 1994). Scrubber devices used include packed or plated columns, and venturi scrubbers. Venturi scrubbers are popular and use a change in gas velocity to shear liquid streams into tiny target droplets into which soluble gases and particulates are transferred. The scrubber accomplishes relatively high velocity by angling the venturi throat (vena contracta), creating greater pressure on the gas into a smaller duct and introducing the sorbent at this point. The polluted sorbent is then
channelled and collected downstream by a mist eliminator (Theodore and Buonicore, 1994).

The problem with the above APCDs is the reliance of air contaminant transfer from one medium (flue gas) to another (i.e. absorbent, adsorbent, baghouse), and later disposed as landfill. With the increase tightening of environmental legislation and regulations of hazardous waste disposal, a more pro-active approach to air pollution control from combustion is the reduction of contaminants. The proposal of reducing criteria pollutants from cement manufacturing is an attractive investigation by focusing on, and restraining, key pollutant-forming mechanisms during combustion and calcination.
Chapter 3: Alternative fuels in cement production

This chapter discusses the use of combustion fuels (both conventional and alternative) for clinker production. It reviews the type, benefit and characteristic of fuels used to meet the combustion needs of a cement plant, while subchapters 3.4 and 3.5 discuss the use of conventional and alternative fuels, respectively. The later subchapter reviews the existing technological and legislative requirements for co-incinerating such alternative fuels. The focus of this chapter is on integration of other fuels into a plant which is designed for certain fuel types, and how this will influence the mechanisms that promote pollutant formation and emission.

3.1 Introduction

Similar to other countries (Jacott et al., 2003; Lechtenburgh, 2015), most of cement plants operating in Australia use powderised coal in the kiln, and petroleum coke in the precalciner vessel. Further to Dellinger et al. (1993) and Sarofim et al. (1994), experimental evidence and technological advances continue to academically support the substitution of these fuel types with other low-carbon resources, with the key decisive characteristics of the PH/PC-kin system being:

1. A high-temperature gas profile is sustained; whereby the material temperature reaches up to 1700 K in the clinkering zone and completely incinerates high-molecular hydrocarbons and PCDD/Fs are dechlorinated (ICF, 2008; Mokrzycki et al., 2003).
2. Residence time at high temperatures are substantial (given the significant kiln length and overall heat exchange) which support the destructive efficiency of hazardous products (Mokrzycki and Uliasz-Bochenczyk, 2003).
3. An alkali environment which neutralises and binds any possible PICs or pollutant-forming catalysts (e.g. PM, chlorine, sulfur, volatiles) from combustion or calcination gases (Giannopoulos et al., 2007a).
4. An oxidising and turbulent atmosphere which forms a highly homogeneous mixture with surplus of O₂ during and after combustion for upstream calcination, and with high gas flow velocities between 12.1-13.5 meters per second (m/s) (Giannopoulos et al., 2007a; Mokrzycki et al., 2003; Karstensen et al., 2006).
5. Immobilisation of trace metals remain to the clinker structure, and the further incineration of fuel with any residuals being absorbed into clinker alleviates any by-product or process waste (Mokrzycki and Uliasz-Bochenczyk, 2003).
6. A large heat exchange surface (with a counter-flow principle) which continually operates with a consistent supply of fuel permits for a high thermal efficiency, and reduces the occurrence of process upset or unsettled conditions (Ali et al., 2011; ICF, 2008; Mokrzycki and Uliasz-Bochenczyk, 2003).

7. The use and effectiveness of costly nitrogen oxide control strategies (e.g. SNCR) whereby the generation of fuel NOx may be available (Saidur et al., 2011a).

With the practise of co-incinerating alternative fuels being relatively mature, Batelle (2002) and Venta (2011) extends on this as sustainable manufacturing with the aid of innovation and integration. As the composition of a fuel can vary dramatically from time-to-time and one place to another, this can have a subsequent effect to the process chemical and physical behaviour. With alternative fuels requiring to have an appropriate chemical content, the knowledge of its composition, structure, reliability, and influence on a combustion system is important so that maximum energy can be acquired while limiting the formation of harmful pollutants. Further to this, Batelle (2002) integrates the progress of knowledge and innovation can only be supported with improved standards and specifications. Throughout the world, various forms of fuels are used in cement manufacturing (EA, 2005b; Karstensen, 2008a and 2008b; Mokrzycki and Uliasz-Bochenczyk, 2003), which can generally include one or more of the following types:

**Solid**
- Black coal (lignite, bituminous, anthracite, pet coke)
- Coal by-products

**Liquid**
- Diesel
- Petroleum products
- Paint residues
- Metal pickling or cleaners
- Lubricating oils
- Distillation residue
- Waste solvents
- Waste oils & resins

**Gas**
- Natural gas
- Process gases
- Pyrolytic gas
- Gasification
- Landfill gas

<table>
<thead>
<tr>
<th>Conventional</th>
<th>Alternative</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solid</strong></td>
<td><strong>Liquid</strong></td>
</tr>
<tr>
<td>Black coal</td>
<td>Paint residues</td>
</tr>
<tr>
<td>(lignite, bituminous, anthracite, pet coke)</td>
<td>Metal pickling or cleaners</td>
</tr>
<tr>
<td>Coal by-products</td>
<td>Lubricating oils</td>
</tr>
<tr>
<td></td>
<td>Distillation residue</td>
</tr>
<tr>
<td></td>
<td>Waste solvents</td>
</tr>
<tr>
<td></td>
<td>Waste oils &amp; resins</td>
</tr>
<tr>
<td><strong>Gas</strong></td>
<td><strong>Liquid</strong></td>
</tr>
<tr>
<td>Natural gas</td>
<td>Paint residues</td>
</tr>
<tr>
<td>Process gases</td>
<td>Metal pickling or cleaners</td>
</tr>
</tbody>
</table>

**Additional Notes**
- Paint residues can include material such as sugar cane bagasse, rice or coconut husks, or wheat or corn straw.
As the energy requirements of a cement plant to produce clinker can also vary dramatically due to the composition of the raw material, this too can have an effect to the behaviour of combustion and subsequent flue gas emissions. Additionally, Neuffer and Laney (2007) identify that the burnability of kiln meal feed can be successful in reducing process energy demands by 15%, which also results in a reduced fuel combustion and pollutant UMEF. There are also additional economic and social benefits which are discussed later.

3.2 Benefits of using Alternative Fuels

Khurana et al. (2002) and Rasul et al. (2005) identify the industries expense of heat and energy through fuel combustion is about 30-45% of the total plant costs. Aside from the apparent economic advantage of some plants currently using 98 ADF% (IEA, 2010a), 5 other sustainable benefits which satisfy the Basel Convention obligations (EIPPCB, 2013; Giannopoulos et al., 2007; Holcim-GTZ, 2006; Supino et al., 2016) can be discussed.

3.2.1 Reducing industry CO₂ emissions

With current demands of carbon-based fuels and no direct government intervention, the path of CO₂ emissions is set to exceed the acceptable 450 Scenario, with the expectation to reach CO₂ concentration levels of 1,400 ppmv in 2050, as seen in Figure 3.1. Even with a highly efficient waste minimisation scenario in today’s society, the increasingly generation of waste materials continues to overburden the demand for its safe disposal. A thesis research by El Atasi (2013) has shown the impact analysis of CO₂ emission by sustainable cement production is at the greatest extent with the co-incineration of ADFs.

![Figure 3.1: Current and projected CO₂ emissions based on coal combustion (Source: CIAB, 2009).](image-url)
3.2.2 Energy recovery, waste incineration or landfill disposal

Similar to the demand of concrete, the generation of waste by-products from industrial processes and society cannot be avoided. As landfill sites struggle to maintain the waste supply and subsequent gases (CH₄) there is a noticeable demand for incineration, however this remains to release similar pollutants through these facilities (Herat, 1994; Venta, 2011). Of the known possible options for pollutant reductions from cement, there is an increasingly demand from industry for the plausible use of ADF which contain low carbon intensities, low CO₂ UMEF, or higher CV so to increase the clinker-fuel ratio. Considerations to these needs should idealise that such possible options are sustainable recovery techniques and not as a proposal to dispose of waste materials.

With the objective to avoid emissions, the benefit of co-incinerating ADF within an existing cement plant for energy aids the reduction of carbon-based fuel consumption and unit mass emissions, along with a cost-effective resource recovery better than that lost by an incinerator. It provides the necessary plant energy-intense demands whilst complying with strict legislative requirements for the complete destruction and irreversible transformation of hazardous pollutants (CSI, 2005; UNEP, 2012). Hogg (2006) reviews the climatic benefits of incinerating several of the above waste types, noting that there are alternative ways to conventional incinerators to generate energy and these can have a positive impact and be publicly acceptable. As seen in Figure 3.2, this consolidation strategy shows the potential on the reduction of net CO₂ UMEF, and would be considered the more environmentally sound disposal option (Cembureau, 2009; Conesa et al., 2008; Greco et al., 2011; IEA, 2010b, Schneider et al., 2011).

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![Figure 3.2: Impact of ADF on overall CO₂ emissions (Source: Cembureau, 2009).](image-url)
The strategy is to maximise the recovery of lost energy from waste incineration or landfill disposal by directly encompassing it into cement production. With this energy, the residual inorganic elements of the alternative fuel are also recovered by the bonding of elements to the clinker crystal, where no remaining liquid, ash or another by-product is produced. The co-incineration of waste serves as a dual purpose while manufacturing cement. This is different to the conventional incinerator or landfill which is to remove hazardous and non-hazardous waste.

Furthermore, the removal a waste source which will undergo decomposing and the subsequent generation of a significant gas stream (e.g. methane from landfill refuge) means this removal is no long required. The cost avoidance from this disposal also benefits with the cheaper marketing of the waste product from other industries, making it more economical for co-incineration than other means of fuel resourcing.

The current sustainable goal of co-incinerating waste in European cement kilns is regulated by the EC (2000) Directive 2000/76/EC, with its coal substitution at about 4.1 million tonnes per year. As seen in Table 3.1, the average fuel substitution rate within EU cement plants is 18 ADF%, with nine EU countries currently exceeding 25 ADF% (Cembureau, 2010; EC, 2000; Giannopoulos et al., 2007a; Rahman et al., 2013; WBCSD, 2010). Standing alone, the Netherlands display an extraordinary example towards environmental sound management with low-carbon fuel substitution within cement plants is currently exceeding 83 ADF% (Cembureau, 2010).

Table 3.1: Countries average percentage substitution of alternative low-carbon fuel within cement plants (Source: EA, 2008; Rahman et al., 2013; WBCSD, 2010).

<table>
<thead>
<tr>
<th>Country / Region</th>
<th>ADF%</th>
<th>Country / Region</th>
<th>ADF%</th>
<th>Country / Region</th>
<th>ADF%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Netherlands</td>
<td>83</td>
<td>Luxemburg</td>
<td>25</td>
<td>Finland</td>
<td>3</td>
</tr>
<tr>
<td>Switzerland</td>
<td>48</td>
<td>Czech Republic</td>
<td>24</td>
<td>Italy</td>
<td>2</td>
</tr>
<tr>
<td>Austria</td>
<td>46</td>
<td>EU (before 2004)</td>
<td>12</td>
<td>Spain</td>
<td>1.3</td>
</tr>
<tr>
<td>Norway</td>
<td>42</td>
<td>Japan</td>
<td>10</td>
<td>Poland</td>
<td>1</td>
</tr>
<tr>
<td>Germany</td>
<td>35</td>
<td>United States</td>
<td>8</td>
<td>Ireland</td>
<td>0</td>
</tr>
<tr>
<td>France</td>
<td>34</td>
<td>Australia</td>
<td>6</td>
<td>Portugal</td>
<td>0</td>
</tr>
<tr>
<td>Belgium</td>
<td>30</td>
<td>Denmark</td>
<td>4</td>
<td>Greece</td>
<td>0</td>
</tr>
<tr>
<td>Sweden</td>
<td>29</td>
<td>Hungry</td>
<td>3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.2.3 **Destruction of hazardous waste**

As quick development propels an emerging economy (like China or India) into the global spotlight, the establishment of hazardous waste infrastructure and BMP is generally not in place. Due to lacking collection, transport and storage facilities, only the easy hazardous waste is recycled and processed while the remaining hazardous waste is disposed in deep burial pits. This limits feasible disposal options for waste-generating industries to engage in a low-cost, environmentally effective practise (Karstensen, 2007). However, the adjoining cement production industry can provide a viable option for the near-complete destruction of hazardous and non-hazardous waste with no significant infrastructure investments needed. Ariyaratne *et al*. (2013b) indicate this with no impacts to clinker quality or emissions during various feed rates of hazardous waste with 30 wt.% wood chips.

This integrated approach serves a useful solution in providing a low-carbon fuel or other means to generate thermal energy, while conserving natural resources, in line with the Basel Convention Annex 4B notation that an operation which may lead to resource recovery, recycling reclamation, direct re-use or alternative uses (UNEP, 2012). With the nature and design of cement manufacturing, the selection and co-incineration of ADF require for some fundamental systematic considerations to be noted so the complete destruction and irreversible transformation of hazardous pollutants is achieved (CSI, 2005; EIPPCB, 2013; UNEP, 2008). An example of this is the disposal of contaminated cattle feed which was responsible to the development of mad-cow disease in 2005, whereby its co-incineration completely achieved complete DRE (CSI, 2005). However, given the economic drivers being strong there is a need for several complex factors to be considered and assessed, particularly the local conditions and statutory policies.

3.2.4 **Resource reduction**

For as long as cement has been produced through the traditional combustion of oil and coal, it would be opportunistic for the industry to consider waste co-incineration as a technological innovation. It just so happens that the double gain that is acquired by this industry would subsequently reduce the demand of other resource and energy producing industries (e.g. coal mining, LNG, oil refinery). A reduction to this industry demand would alleviate the dependability and strain which currently exists on the infrastructure for resource access, extraction, handling and transportation (including its shipping). This
relief would subsequently benefit the socio-economic component of communities which are currently impacted by resource developments.

3.2.5 Induced economics

For cost optimisation, the economic benefit to incorporating alternative fuels into cement production needs to be of considerable value. Capital investment may be required to include technological equipment or plant upgrades, and the compatibility of a specific alternative fuel will be a key determinant to this need. This additional cost potential is evident in case where boilers or heaters integrate the use of ADFs. Supporting this feasibility is the subsequent fuel-cost saving which can be achieved, and the degree of substitution. The higher the CV and ADF%, the greater the cost saving per unit of product. Saidur et al. (2011b) review of biomass substitution in boilers showed a consistent and proportional cost savings with an increasingly ADF substitution.

A fundamental element to cost-savings is the initial price of conventional fuel against a reduced cost of the fuel substitute. As current coal resources are globally abundant and diverse, the associate cost is relatively low at €2.34 - 2.51 for petcoke or coal (Barker et al., 2009), however the general cost associate with alternative fuels is also comparatively low. Worrell et al. (2008) and Barker et al. (2009) notes that, based on a LHV-basis the total fuel cost is about €8 per clinker tonne (with a total plant cost of up to €21 per clinker tonne), and with the use of alternative fuels that achieve an energy saving of 0.6 gigajoules per tonne (GJ/tonne) clinker, it reduces the capital costs by €1 and a CO₂ UMEF reduction of 0.076. Where alternative fuels have an energy saving >0.6 GJ, up to €3.7 per clinker tonne can be saved and the CO₂ UMEF is reduced by up to 0.012. Worrell et al. (2008) identifies that where a conventional plant can incorporate free-costing fuel to a 30% thermal substitution rate, and if technological upgrades are not required then it could save up to €2.4 million.

Importation costs associated with conventional fuels will significantly change as supply demands increase and resource volumes decrease. Of considerable value is when the option to co-incinerate localised, high-CV hazardous waste material (e.g. spent carbon, waste solvent, waste oil) when it is available, as the subsequent recycling, incineration or deep-burial costs could be relatively high. Queiroz Lamas et al. (2013) identified a 1.5 million tonnes per annum (mtpa) manufacturing plant in Balsa Nova, Brazil, will have an
annual savings of US$ 1.415 million from the 15 wt.% replacement of petroleum coke with an alternative waste fuel.

For fuel transportation and handling, the initial capital cost will most likely be fixed and existing to normal plant operations, and any additional costs associated with ADF co-incineration will vary and be largely dependent on several variables including distance, compatibility, and regulatory requirements. Under typical situations, and in support to the above-mentioned benefits, is that an ADF is generally sourced within a proximity of a cement plant. In-turn, this results in the co-incineration of alternative fuels to be more economical than landfill or incineration options, particularly for hazardous waste. An economic and environmental evaluation by Baidyaa et al. (2016) showed co-incineration to be the most effective waste disposal technique to these other options.

There is however, the additional electrical energy and potential cost required for the preparation and handling of alternative fuels within cement manufacturing. Further to the average 4 or 5% of plant electrical energy for coal grinding and handling, the substitution of ADF as a secondary fuel does not completely subsidise the equivalent energy use. This additional energy (depending on the ADF type, per cent substitution and the extent of incineration) is required to provide a uniform heating effect to the plant, and can increase this fuel handling and preparation demand up to 6 or 7%.

As a resource commodity, and the expense associated with its access and extraction, conventional fuels (gas, oil, coal) are economically dearer due to regulatory performance and emission targets, and the infrastructure required for external power generation is an expensive commitment. Thus, manufacturing costs for clinker production with co-incineration are reduced as alternative fuel are cheaper. Finally, plant operating and maintenance costs also need consideration as these are greatly influenced by technological devices, effects and variability of fuel and alternative fuel types, and the process alternations to maintain clinker characteristics.

3.2.6 Conclusion

With the above examples of remarkable acceptance and integration of thermal energy replacement, it is evident that cement manufacturing can maintain sustainable practises while utilising 100 ADF% substitution. However, caution and science needs to be exercised, as the incorrect preparedness and alignment of fuel co-incineration outside of process designed parameters could adversely constitute a threat to humans and the
environment (EEA, 2005; Karstensen, 2004b; Karstensen et al., 2005). Potgieter (2012) review of how sustainable co-incineration is signifies the greatest energy efficiency will be achieved through a 4-5 cyclone PH/PC/kiln with electricity generated from ADF types (e.g. tyres, used solvents and oils) and a waste heat recovery unit.

As the ADF-integrating countries represent the minority of global cement manufacturing industry, there remains a considerable challenge with the predominate concrete-producing countries (like China and India) whereby almost 90% of energy is sourced from coal, and the substitution of alternative fuels for thermal energy production is significant low at less than 1 ADF% (Degré, 2014; Fonta, 2014). Studies by Hasanbeigi et al. (2010) and Price et al. (2009) showed 16 new PH/PC-kilns in China’s Shandong Province utilizing no alternative fuel materials despite Chinese law now encouraging its use, and its potential and availability could realistically extend up to 100 ADF%. Studies by Price et al. (2009) and Morrow et al. (2013) also showed cement plants to have a typical energy saving of 0.6 GJ per clinker tonne, with no impact to the rate of clinker and no additional cost to the plants’ annual operations or maintenance. Essentially it would be these key areas which would have the greatest influence on the global reduction of CO₂ and hazardous air pollutants, which would increase the global substitution of base fuels in cement plants past the current 0.5 ADF%. A key fundamental issue with dominating countries is the imbalanced supply-demand from thousands of cement plants, making them somewhat unsustainable or non-compliant (Barker et al., 2008; Supino et al., 2016).

Numerous publications have been compiled on this very topic with the objective to help address this thermal substitution shortage by providing technical examinations, experimental outcomes and action plans. With the development and promotional awareness of the roadmap visions (IEA, 2009 and 2010a and 2013), estimates have identified that with a 2050 low carbon economy, the global cement manufacturing industry could be supported by 60 ADF% (including biomass) substitution, which would also result in global decrease of 27 vol.% in fuel-based CO₂ emissions (Cembureau, 2013 and 2014; Goisis, 2014).

3.3 Characteristics of Fuels

Previous experimental trails (EIPPCB, 2013; Holcim-GTZ, 2006; UNEP, 2008) have shown some evidence that the type and amount of substituted waste fuel can have a
substantial influence on a combustion system. This can be determined by the selected ADF feed location, the amount of oxidiser and heat needed, and the structural make-up (and control) of the flue gas due to the plant design. However, a further important determinant to a plant’s capacity to successfully operate is the fuel’s composition and thermodynamics, and these technical properties should be examined before co-incineration. This is established by several publications (Mokrzycki and Uliasz-Bochenczyk, 2003; Mokrzycki et al., 2003; Madlool et al., 2011; Rahman et al., 2013; UNEP, 2008; Willitsch et al., 2003) and predominately includes:

- Physical state and properties (such as compatibility, homogeneity, particle size and suitability, density, ash content, humidity of <20 wt.% H₂O, grindability).
- Chemical composition, toxicity and circulating elements (including organic compounds at <50 ppmv, total heavy metals at <2,500 pm (with Cl₂ at <0.2 wt.%, sulfur at <2.5 wt.%; Hg at <0.4 wt.%), and volatiles).
- Minimum kiln fuel calorific value (Kₜ) of 18 MJ/kg (or 14 MJ/kg weekly average).
- Minimum precalciner fuel calorific value (PCₜ) of 10 MJ/kg.

VDZ (2012) add further to this with particle sizing being preferred to a 2-dimensional structure (<30 mm edge length) and a bulk density of 0.1-0.2 t/m³. As shown in the introduction of this chapter, various forms of alternative fuel are currently used or available to cement manufacturing, and its compatibility and homogeneity needs to be examined, evaluated and maintained so that impacts to clinker production are minimised and that complete thermal destruction is achieved. With numerous types of alternative fuels containing large solid particles, sufficient preparation (e.g. drying, sorting, shredding, compressing) or gasification may be required so that a homogeneous fuel is supplied and devolatilisation can occur (subchapter 2.5.1). This physical state of this material is of significant to other cement plant components and equipment required, namely its transportation, storage, handling, and feeding.

The volatile content (e.g. alkalis, chlorine, sulfur, sodium, potassium) of a fuel is also equally important at various stages of the process, as its integration with the raw meal has a direct effect to the formation of salts (e.g. potassium sulfate (K₂SO₄), sodium sulfate (Na₂SO₄)). This formation can result in reducing combustion conditions (e.g. fast fuel ignition), ring development in the kiln inlet zone, blockages to the PC vessel or PH cyclones, irregular material flow, heat loss or corrosion (del Mar Cortada Mut et al., 2015; Pipilikaki et al., 2005; Zaka et al., 2014). Furthermore, Reijnders (2007) highlights the
use of RDF and municipal solid waste (MSW) can introduce chlorine into the kiln and increase the volatility of certain metals, particularly Cd, Hg and Pb.

Water in combustion systems is either released from fuel containment or formed by the oxidisation of fuel hydrogen. Its presence (immersed in both fuel or raw meal) absorbs the energy needed to evaporate with increasing temperatures. Generally speaking, the moisture content of fuel is required at < 20 wt.% as of these have a varied amount amongst its chemical elements (Mokrzycki and Uliasz-Bochenczyk, 2003), and this has an influencing effect on the size, design, and operation of the system and, consequently, the selected APCD. High moisture fuels can affect the operating capacity of the combustion flame and its sintering stage, and are generally limited to be used as secondary fuels at the precalciner due to the required aid of pre-combustion drying.

The presence of metal compounds in fuel is shown to be effectively incorporated into the clinker material or contained by an appropriate APCD. Where key plant conditions are maintained, numerous studies showed similar metal emissions (excluding Cd and Hg) during normal operations and co-incineration (Conesa et al., 2008; Giannopoulos et al., 2007b; Willitsch et al., 2003). Mentioned above, Cd and Hg are highly volatile with the presence of chlorine, and partition more readily into the flue gas. Similar to the presence of circulating metal elements (such as, Cd, S, Na, K), the key effective control is by limiting their concentration in the raw meal or fuel (Mokrzycki et al., 2003).

As an important element, the heating release value (or CV) of fuel predominately establishes the size and operation of combustion based on how much fuel is to be burnt so to produce the desired heated material. Cement plants are typically sized and designed to the CV of the intended fuel and material to be used, and the required energy. The CV of solid fuels have increased significantly over the past years, as additional amounts of product and general wastes are somewhat being incorporated as a supplied fuel (Baukal, 2004; CSI, 2005; UNEP 2008). Thus, the CV of this substituted fuel will be required to engender the demand of the fuel it is replacing, without it being a large increase in mass as this may introduce additional handling, feeding and stoichiometric problems.

3.3.1 Suitability of fuel types to cement plant needs

From the above notations, Table 3.2 identifies the general LHV, HHV and CO₂ equivalent emissions factor of various conventional and alternative fuel types. The values are sourced from literature reviews, and are an approximate due to localised conditions
(e.g. activity or process source, weather, moisture, disposal restrictions). Where CO₂ emission intensity calculations are needed for coal and petroleum coke, this is based on:

\[
\text{CO}_2 \text{ emission intensity} = \text{CC} \times 3.67 / \text{HHV} \tag{3.1}
\]

where CC = carbon content of fuel (kg of carbon per tonne of fuel)

For the calculation of the CO₂ emission intensity for alternative fuels is based on:

\[
\text{CO}_2 \text{ emission intensity} = \text{CC}_{ADF} \times 3.67 / \text{HHV} \tag{3.2}
\]

where \(\text{CC}_{ADF} = \text{total carbon content} - \text{ADF carbon content}\) (kg of carbon per tonne of fuel)

For an assessment to the suitability of fuel options for cement production, the next few subchapters will review the characteristics of key and current conventional and alternative fuels. Outside of these selected types, other fuel options may also be available and may also result as substitutes for the reduction of CO₂ emissions.

### 3.4 Conventional Fuels used in Cement Manufacturing

#### 3.4.1 Solid

The type of solid fuels used in cement manufacturing predominately includes black coal and coal by-products, which is a complex substance with a varying chemical, molecular and physical consistency, and naturally contains remnants of moisture, nitrogen, sulfur, oxygen, fluorine, ash, and trace metals. The classification of coal is according to its calorific value, ranging from lignite (low CV, high volatile and inert moisture content) to anthracite and petroleum coal (high CV, low VM and inert moisture content). As seen in **Table 3.2**, lignite generally contains a heating range of 23-32 MJ/kg and moisture content of 34 wt.%, whereas anthracite or petroleum coal contain a higher heating range of 27-35 MJ/kg and lower moisture content of 2-3 wt.%. Bituminous coal is abundant, readily available and is widely used in cement kilns. For the general composition of these coal classifications, they predominately have a high content of carbon (67-87 wt.%), hydrogen (2-5 wt.%), oxygen (1-20 wt.%) and sulfur (1-5 wt.%). Some additional combustion properties include swelling, ash content (low, medium or high), or trace elements of sulfur, chlorides or nitrates (Alsop, 2014; Greco et al., 2011).
Table 3.2: General proximate & compositional analysis, calorific value, and CO₂ UMEF with conventional and alternative fuels in cement production

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<tbody>
<tr>
<td></td>
<td>VM</td>
<td>FC</td>
<td>Ash</td>
<td>IM</td>
<td>C</td>
</tr>
<tr>
<td>Lignite</td>
<td>32</td>
<td>52</td>
<td>20</td>
<td>34</td>
<td>67</td>
</tr>
<tr>
<td>Coal by-product</td>
<td>20</td>
<td>69</td>
<td>11</td>
<td>1.3</td>
<td>75</td>
</tr>
<tr>
<td>Bituminous¹¹</td>
<td>14-57</td>
<td>53-86</td>
<td>11</td>
<td>3</td>
<td>70-74</td>
</tr>
<tr>
<td>Anthracite</td>
<td>2-14</td>
<td>86-98</td>
<td>15-19</td>
<td>3</td>
<td>72-87</td>
</tr>
<tr>
<td>Pet coke¹¹</td>
<td>10-14</td>
<td>82-89</td>
<td>0.5</td>
<td>1-6.3</td>
<td>82-90</td>
</tr>
<tr>
<td>Domestic oil</td>
<td>83</td>
<td>~ 0</td>
<td>0-0.3</td>
<td>85</td>
<td>11-13</td>
</tr>
<tr>
<td>Natural gas</td>
<td>77</td>
<td>~ 0</td>
<td>~ 0</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>Wood-waste (mainly pine)</td>
<td>70-85</td>
<td>10-18</td>
<td>0.3-6</td>
<td>2-10</td>
<td>42-52</td>
</tr>
<tr>
<td>RDF &amp; MSW</td>
<td>64-81</td>
<td>4-4-14</td>
<td>8-28</td>
<td>3-25</td>
<td>42-47</td>
</tr>
<tr>
<td>Cardboard &amp; paper residues</td>
<td>73-88</td>
<td>6-12</td>
<td>1-25</td>
<td>1-10</td>
<td>39-52</td>
</tr>
</tbody>
</table>

¹¹ Most utilised coal-type fuel in the cement industry
<table>
<thead>
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<tbody>
<tr>
<td></td>
<td>VM</td>
<td>FC</td>
<td>Ash</td>
<td>IM</td>
<td>C</td>
</tr>
<tr>
<td><strong>Plastics</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethylene</td>
<td>99-100</td>
<td>~ 0</td>
<td>~ 0</td>
<td>0-2</td>
<td>84-86</td>
</tr>
<tr>
<td>PVC</td>
<td>95-98</td>
<td>4.8-6</td>
<td>0.4</td>
<td>0-2</td>
<td>38-41</td>
</tr>
<tr>
<td>non-chlorinated</td>
<td>83</td>
<td>8</td>
<td>6</td>
<td>2</td>
<td>60</td>
</tr>
<tr>
<td><strong>Alternatives</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bio-solids</td>
<td>67</td>
<td>15</td>
<td>4-20</td>
<td>10-28</td>
<td>35-40</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>50-85</td>
<td>0-5</td>
<td>15-26</td>
<td>5.2-7</td>
<td>28-40</td>
</tr>
<tr>
<td>Spent carbon</td>
<td>4</td>
<td>23</td>
<td>71</td>
<td>0.6</td>
<td>26-36</td>
</tr>
<tr>
<td>Biomass</td>
<td>75-80</td>
<td>16</td>
<td>4</td>
<td>8</td>
<td>43-54</td>
</tr>
<tr>
<td>Waste solvents</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>10-12</td>
<td>38-46</td>
</tr>
<tr>
<td>Waste oil</td>
<td>-</td>
<td>~ 0</td>
<td>~ 0</td>
<td>&lt;5</td>
<td>70-86</td>
</tr>
</tbody>
</table>
Coal by-products vary in composition, and include incremental elements of materials (wood chips, plastics) or waste, enhancing the economic value of fuel (particularly with the CV of lignite) or to eradicate the waste. If used, these are generally combined with petcoke as it is the most widely utilised pulverised fuel in the kiln and precalciner, however it can have difficulties in flame temperature and residence time due to larger particle sizes and possible combustion rings being formed (Bhatty et al., 2004). Due to the higher composition of nitrogen in petcoke, its use and NO\textsubscript{x} formation is only increased in comparison to fuel oil.

Some heavy metals (e.g. Sb, As) and halogens are also found in petcoke (Mantus et al., 1992; Bhatty, 2011), and due to their low concentration and/or volatility, these compounds are typically captured within the clinker product or CKD, and not readily released in the flue gas. Karstensen (2007) discusses this further with the notion that the presence of metals, halogens, and organic compounds can complicate the emission contribution from co-incinerating hazardous waste materials. A mass balance review by Yan et al. (2015) showed some metals (As, Hg, Se) to vary between kilns with its input composition being source by raw meal or combustion fuel (i.e. lignite), with Hg compounds being volatised early and released as opposed to As and Se which was shown to be contained within the clinker product or APCD. A study by Air Control Techniques (2002) reviewed emissions from 35 cement plants with conventional coal, reporting an average Hg concentration of 28 µg/Sm\textsuperscript{3} (7% O\textsubscript{2}), with variations from baghouse units (39.5 µg/Sm\textsuperscript{3} (at 7% O\textsubscript{2})) and ESP units (10.6 µg/Sm\textsuperscript{3} (7% O\textsubscript{2})).

### 3.4.2 Liquid

Fuel oil and diesel are the two primary liquid fuels used in combustion systems. The most common process of liquid combustion is where the fuel is atomised to produce and mix small droplets with hot air. Fuel oil is burned as a suppression of air-oil droplets into the flame zone, and is heated by flame radiation and the convention of surrounding hot gases. As the required oxygen for diffusion is dependent on its surface area, the flame time of oil sprayed into a system should be proportional to the droplet diameter squared, and the mass on diameter cubed. As the oil particle mass and diameter increased, the time required to burn will also increase (Alsop, 2014). For heavy crude oils, by raising the temperature to greater than 100 \textdegree C is shown to significantly reduce the viscosity of the oil, and thus increases the proportion of complete combustion. Due to its high carbon-
hydrogen content, the light components of oil will vaporise and ignite, while the heavier droplets may only partially vaporise, leaving a residual coke particle as a PIC.

3.4.3 Gas

Natural gas is the cleanest conventional fuel, and is used fuel at the kiln’s primary burner due to its availability, consistent flame momentum and its low cost. Gas fuels predominately contains pure CH\textsubscript{4} with amounts of ethane, nitrogen, helium, carbon dioxide, and traces of hydrogen sulfide and mercaptans. By-products of natural gas used as a fuel can contain butane and propane, with traces of butylene. Due to its lower carbon content (being predominately hydrogen), the use natural gas generally requires a more turbulent profile with a mixing of 10-15 vol.% more combustion air than other fuels, equally requiring more radiant heat for calcination and producing 10-15 vol.% more flue gas pollutants. However, when compared with the same thermal energy production, natural gas can emit 31 vol.% and 38 vol.% less CO\textsubscript{2} than fuel oil and coal, respectively (Alsop, 2014; Bhaty \textit{et al.}, 2004).

3.4.4 Use of coal for heat and energy

Evidence shows that despite the global awareness and integration of environmentally-focus political protocols, there is an increasing production and use of carbonaceous fuels (specifically coal and lignite) for the generation of electricity (currently at 41%) and primary energy consumption (currently at 30.1%) (WCA, 2014). With coal being readily abundant and widely dispersed throughout the world, its extraction in 2013 hit at a record level of 7,822.8 Mt/yr and is shown to have expanded at a rate of 46-67 wt.% over the past 25 years (Sajwan \textit{et al.}, 2006; WCA, 2014).

With energy demands set to double by 2035, and the availability of coal reserves (between 892 to 1052 billion tonnes) able to provide the current extractions for over 113 years. With this, the probability of the 450 Scenario being achieved and sustainable seems to be highly unlikely, unless future energy generation is achieved with 25% of todays’ current conventional fuel usage (CIAB, 2009 and 2013; BP, 2014; WCA, 2014). Within the international community there remains doubt of 450 Scenario being achieved, as there is great reliance on China to improve imminent energy practices and fuel switching by 58.4%, as well as an increasing (and future global dominant position) presence with Indian cement manufacturing (CIAB, 2009 and 2012).
Even with energy efficiency improvements, consideration must be granted however to the combustion of coal and the offset carbon emissions that it produces. In 2012 for example, the primary energy consumption of coal was at 29% yet it was also accountable for about 44 vol.% of global CO₂ emissions (Figure 3.3). When compared to other fuel types, coal has an approximate 180 vol.% increase to the CO₂ emissions released through the combustion of oil and natural gas, predominately due to its higher carbon content. Furthermore, when referenced against more carbon-neutral fuels (including biofuels and waste), the release of CO₂ emissions from coal was over 3,000 vol.% higher which further supports the importance of fuel switching investigations.

![Figure 3.3: World primary energy consumption and CO₂ emissions, by fuel in 2012 (Source: IEA, 2014a).](image)

Since the employment of the UNFCCC Kyoto Protocol in 2005, the data presented by the IEA (2014b) on global Energy Information shows most EU and OECD countries to have a stagnate or decreasing trend in conventional fuel consumption. Table 3.3 shows the fuels used for electricity and heat production (in petajoules (PJ)) during 2012 from the top major conventional fuel producers, however more global action is required as the OECD Asia and OECD Europe regions remain with a rate increase (between 1973 and 2012) of their electricity intensity index of 0.4% and 0.1% respectively (IEA, 2014b). Table 3.3 also shows the gross electricity production (in TWh) during 2012, partly of which 62.8% was provided from combustible fuel (made up of conventional-fuel-fired plants (60 wt.%)) and of biofuel-waste plants (2.8 wt.%)). Between 1973 and 2012, global production increased from 6142 TWh to 22752 TWh (an annual rate of 3.4%). For the combustion of all conventional fuel types, the global electricity production during 2012 was at 67.7%.
Table 3.3: Fuel use for cement manufacturing in 2012 by major countries, gross electricity production and coal consumption (Source: IEA, 2014b).

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<tbody>
<tr>
<td>China</td>
<td>42508</td>
<td>505.4</td>
<td>221.4</td>
<td>995</td>
<td>504.7</td>
<td>198.2</td>
<td>0.9</td>
<td>44933.9</td>
<td>3916.16</td>
<td>97.39</td>
<td>-</td>
</tr>
<tr>
<td>United States</td>
<td>7496.4</td>
<td>9520.2</td>
<td>435.3</td>
<td>72.7</td>
<td>275</td>
<td>138.7</td>
<td>138.7</td>
<td>26768.7</td>
<td>2941.05</td>
<td>78.9</td>
<td>73.88</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>1336.3</td>
<td>766.3</td>
<td>67.6</td>
<td>13.3</td>
<td>46.8</td>
<td>72.6</td>
<td>72.6</td>
<td>2371.5</td>
<td>247.33</td>
<td>17.08</td>
<td>20.47</td>
</tr>
<tr>
<td>Russia</td>
<td>1896.3</td>
<td>10103.3</td>
<td>38.5</td>
<td>146.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>14040.5</td>
<td>722.37</td>
<td>-</td>
<td>177.53</td>
</tr>
<tr>
<td>India</td>
<td>8660.7</td>
<td>740.5</td>
<td>443</td>
<td>-</td>
<td>21.5</td>
<td>15.9</td>
<td>12109.2</td>
<td>9117.97</td>
<td>372.24</td>
<td>-</td>
<td>18.17</td>
</tr>
<tr>
<td>Germany</td>
<td>1139.9</td>
<td>72.3</td>
<td>712.7</td>
<td>151.6</td>
<td>199.7</td>
<td>194.8</td>
<td>4125.5</td>
<td>371.66</td>
<td>51.18</td>
<td>54.58</td>
<td>67</td>
</tr>
<tr>
<td>Saudi Arabia</td>
<td>-</td>
<td>1682.8</td>
<td>1384.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3067.6</td>
<td>271.68</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>South Africa</td>
<td>2512.1</td>
<td>2 -</td>
<td>4.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2518.4</td>
<td>2518.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Australia</td>
<td>331</td>
<td>36.3</td>
<td>464.1</td>
<td>12.8</td>
<td>-</td>
<td>15.6</td>
<td>2299.5</td>
<td>224.91</td>
<td>214.55</td>
<td>2.34</td>
<td>3.17</td>
</tr>
<tr>
<td>Indonesia</td>
<td>-</td>
<td>384.7</td>
<td>431.7</td>
<td>2.6</td>
<td>0.9</td>
<td>-</td>
<td>1945.8</td>
<td>144.77</td>
<td>146.76</td>
<td>10.16</td>
<td>8.66</td>
</tr>
<tr>
<td>Poland</td>
<td>992.9</td>
<td>23.3</td>
<td>63.6</td>
<td>106</td>
<td>0.9</td>
<td>3.7</td>
<td>1755.5</td>
<td>104.18</td>
<td>29.4</td>
<td>105277.2</td>
<td>62723.4</td>
</tr>
<tr>
<td>Kazakhstan</td>
<td>818.3</td>
<td>7.8</td>
<td>137.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>972.9</td>
<td>600.4</td>
<td>600.4</td>
<td>600.4</td>
<td>600.4</td>
</tr>
<tr>
<td>OECD Total</td>
<td>18548</td>
<td>3670.1</td>
<td>21209.5</td>
<td>2076.6</td>
<td>184.8</td>
<td>1059.1</td>
<td>62723.4</td>
<td>62723.4</td>
<td>62723.4</td>
<td>62723.4</td>
<td>62723.4</td>
</tr>
<tr>
<td>Non-OECD Total</td>
<td>59884</td>
<td>803.1</td>
<td>27674.3</td>
<td>346.2</td>
<td>104</td>
<td>29.4</td>
<td>105277.2</td>
<td>105277.2</td>
<td>105277.2</td>
<td>105277.2</td>
<td>105277.2</td>
</tr>
<tr>
<td>World</td>
<td>78433</td>
<td>20122</td>
<td>209.4</td>
<td>1718</td>
<td>12546</td>
<td>3763.6</td>
<td>530.9</td>
<td>168000.6</td>
<td>629.8</td>
<td>168000.6</td>
<td>168000.6</td>
</tr>
</tbody>
</table>

12 Includes hard coal, brown coal, peat, oil shale & sands, coal gases, oil products & natural gas.

13 Includes wood, wood-waste, solid waste, industrial & municipal waste, biogases & liquid biofuels.

14 Estimated data.
As Australia is the ninth-largest energy producer (and is one of only three net energy exporters in the OECD), its annual energy consumption is equally increasing at a rate of 33% over the past decade (IEA, 2012) with coal being the primary fuel to generate 77% of the electricity and heat needs (IEA, 2014b; Sajwan et al., 2006). For the consumption of electricity for industries, it remains relatively constant (44.2% of 52.5 TWh in 1973, and 38.2% of 209.3 TWh in 2012) with economic and population growth (IEA, 2014b). More specifically to cement manufacturing with the non-metallic minerals sub-sector, it currently accounts for between 6.3 and 7.2 percent of the global industrial energy usage, and is subsequently accountable for about 5 vol.% of the global anthropogenic CO₂ emissions. The historical consumption of energy and electricity to this sector within Australia can be seen in Table 3.4 (IEA, 2007a and 2014b).

**Table 3.4:** Consumption of energy and electricity in Australian non-metallic subsector (Source: IEA, 2014b).

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total energy consumption [Mtoe]</strong></td>
<td>0.63</td>
<td>2.05</td>
<td>2.14</td>
<td>2.03</td>
<td>2.51</td>
<td>2.63</td>
<td>2.68</td>
<td>2.47</td>
</tr>
<tr>
<td><strong>Electricity consumption [Mtoe]</strong></td>
<td>-</td>
<td>0.18</td>
<td>0.25</td>
<td>0.3</td>
<td>0.38</td>
<td>0.4</td>
<td>0.41</td>
<td>0.39</td>
</tr>
<tr>
<td><strong>Electricity consumption [TWh]</strong></td>
<td>-</td>
<td>2.05</td>
<td>2.92</td>
<td>3.49</td>
<td>4.47</td>
<td>4.68</td>
<td>4.76</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Successful tracking of implementing 450 Scenario is identified by process indicators (Table 3.5) which support key milestones and planning goals. Covering each pillar, these objectively aim to identify performance and achievements, whilst also guide what risks are apparent or what developments are needed to achieve the set targets (IEA, 2010a).

**Table 3.5:** Scenario 450 process indicators (Source: IEA, 2010a)

<table>
<thead>
<tr>
<th></th>
<th>2012</th>
<th>2015</th>
<th>2020</th>
<th>2025</th>
<th>2030</th>
<th>2050</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Energy consumption per clinker [GJ/tonne]</strong></td>
<td>3.9</td>
<td>3.8</td>
<td>3.5-3.7</td>
<td>3.4-3.6</td>
<td>3.3-3.4</td>
<td>3.2</td>
</tr>
<tr>
<td><strong>ADF% &amp; biomass usage</strong></td>
<td>5-10%</td>
<td>10-12%</td>
<td>12-15%</td>
<td>15-20%</td>
<td>23-24%</td>
<td>37%</td>
</tr>
<tr>
<td><strong>Clinker to cement ratio</strong></td>
<td>77%</td>
<td>76%</td>
<td>74%</td>
<td>73.5%</td>
<td>73%</td>
<td>71%</td>
</tr>
<tr>
<td><strong>CO₂ UMEEF</strong></td>
<td>0.75</td>
<td>0.66</td>
<td>0.62</td>
<td>0.59</td>
<td>0.56</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Based on data provided in Table 1.5 (IEA, 2014b), being 1,770.7 PJ from coal fuels out of a total 2,299.5 PJ from all fuel types.
3.5 Combustion of Alternative Fuels

With the social and industrial creation of by-products from manufacturing, construction, process, and communities, the typical reference of this material is waste. This can occur even when the product is recovered and used as an alternative low-carbon fuel, for example the generation and recovery of thermal energy through the co-incineration of waste oil. The beneficiary use of co-incineration a waste product into a resource-intensive process not only can provide an equal source of thermal energy substitution, it also contributes several benefits to society in waste management practices and cement economics, industry competitiveness and accountabilities, and the receiving human and environmental health impacts (Degré, 2014).

The integration of waste into kilns is well aligned as the CV of the ADF is used to substitute the conventional fuel while integrating any PIC or inorganic components into the clinker. Through a life cycle analysis, the co-incineration of certain ADF can reduce the need for external incetration or land fill, and their subsequent release of GHG emissions or disposal of hazardous ash content (ICF, 2008; IEA, 2007b and 2010a; IPP, 2014). Galvez-Martosa and Schoenbergerb (2014) utilise this tool for the environmental evaluation of this treatment technique, highlighting that subsequent CO₂ and heavy metal emissions are not of significance given the initial amount of pollutants in the input is increased. However, if improper handling and use of waste co-incineration occurs this can introduce and form new pollutants (e.g. SO₃, PAH, dioxins) where elements were either not initial present or were at relatively low levels. Munster and Lund (2009) supports this, but also adds that the worst solution would be the complete loss of potential energy sourced from unusable waste materials.

Kääntee et al. (2004) notes that as these fuel types can be in various forms (from course to powderised solids, or viscous to unsolidified liquids), their state may need additional drying and treatment so its physical handling can achieve a stable, homogenous fuel supply into the system. The following subchapters look at the general types of alternative fuels currently available or utilised, with a brief review of its compositional analysis (further to the detail provided in Table 3.2), required treatment and handling practises, influences to cement plant parameters or other pollutant-formation, capability to the APCDs, and the expected emissions from its co-incineration.
3.5.1 Solid

3.5.1.1 Paper and wood waste

Waste paper and wood can be explicitly sourced from industrial or residential, or both. A study by Encycle Consulting (2013) identified these waste types can be sourced within Australia from various industry sectors, particularly construction/demolition, retail, timber milling, paper and pulp, and furniture manufacturing; with the total generation of 4.278 and 0.775 million tonnes for cardboard-paper and timber waste streams, respectively. With the raw material for most of these industries being either hardwood or softwoods, the chemical and physical properties of the final waste product can vary (Sørum, 2000). Uncontrolled, or co-mingled, waste from both industrial and residential typically end up within municipal facilities. From forestry activities, Walker et al. (2009) signifies how wood chip residues are sustained in a growing economy, whereby its continued economical supply of this alternative fuel can be maintained within a growing economy, making an abundant and readily-available energy source. The study further reports on the ash contributions to clinker material from the co-incineration of waste wood products (Albino et al., 2011), with no additional changes to air emissions.

With limited literature published on the sole co-incineration of paper or wood waste, its composition will generally have a low-ash high-moisture content, LLV of 14-18 MJ/kg, and a significant volatile content (70-88 wt.%) which formulates considerable NOx, TVOCs and PICs (particularly CO, PAHs, dioxins, and PCBs). Even though it has a comparatively low heating value, its low carbon content should provide a considerable reduction in the CO2 UMEF. If resourced from municipal facilities, it will generally be co-mingled with some plastic content, which may present some drying challenges prior to shredding it into a manageable fuel type. The sulfur content in wood waste and other biomass fuels (<0.2 wt.%) is significantly less than coal or oil, and influences the gaseous formation of SO2, K2SO4, and Na2SO4 in the gas phase (del Mar Cortada Mut et al., 2015). However, the chlorine content in wood and paper materials (~0.8 wt.%) can have a greater contamination (e.g. PAH) or increase heavy metal volatilisation (e.g. Hg) when compared to other carbonaceous fuels. For PCDD/F, the use of wood contaminated with other substances (e.g. paint, preservatives, pesticides) can subsequently increase pollutant formation due to the presence of catalytic metals or chlorinated organics (Murray and Price, 2008). A study by CSI (2005) showed no increase in metals, organics (including
PCDD/F) or NO₂ emissions during the co-incineration of demolition timber in a cement kiln.

These materials can be used as the primary fuels or co-combusted at either the kiln burner or precalciner, with the necessary drying and particle sizing (from shredding) to be achieved prior to its use (Willitsch et al., 2003). Due to the general nature of its extensive and locality supply (like RDF), the logistical haulage of paper and wood material are of shorter distances and simplified shipments. These materials are easily transported to the selected burner and are heterogeneous with other fuel types. Ariyaratne et al. (2013c) examined the co-incineration of hazardous waste (solvents, paint and glue) with wood chips and plastic at varying ADFₚ (between 10.3-68.8% weight basis), showing the most optimal being at 52% coal energy equivalent (based on CO and NOₓ emissions). Rodrigues and Joekes (2011) identify that under adequate conditions, waste oil, solvent, tyres, and refuge derived fuel (RDF) are a useful supplementary fuel, whereby concrete product can encapsulate certain materials like tyre, plastic or glass. Even if these materials are a more economical viable resource, their use still require to provide evidence of a safe and complete destruction of concerning POPs.

The additional use of paper or treated wood is shown to be compatible to existing plant APCDs due to the materials’ composition and high combustion capacity, however an offset of increased fly ash content and the presence of other chemical compounds as previously mentioned, such as sulfur, chlorine and heavy metals.

3.5.1.2 Refused derived fuel from municipal solids waste

As a fundamental product to a growing human population and urbanisation, the composition of RDF from MSW will vary due to source locations, segregation and recycling techniques. Becidan (2007) identifies the increasing MSW volumes and diversification being due to an increasing population and the propagation of a modernised style of living. The European Commission (2003) reports RDF is generally produced through separation and screening of MSW, shredding, blending, and drying for later processing or packaging. Kara et al. (2008) identify the characterisation of RDF input to approximately contain paper (25 wt.%), textiles (17 wt.%), organics (22 wt.%), plastic (15 wt.%), glass and in some cases, scrap metal or carpet. After segregation, the remaining
material for use can account for 20-60 wt.% of the initial RDF input (Kara *et al.*, 2008; Murray and Price, 2008).

Variance to this content can therefore have great influences on physical and chemical properties, particular with CV, ash, N₂, Cl₂ (0.2-1.3 wt.%), sulfur (0.2-0.4 wt.%), and high moisture (40-50 wt.%). With varying reports on the thermal energy of RDF being 14-25 MJ/kg, Genon and Brizio (2008) note that its range can be heavily influenced by the inclusion of rubber or plastics preferably due to beneficial HHVs ranging from 30-40 MJ/kg (Alsop, 2014; CSI, 2006; EC, 2003). With these varying influences in mind, Zhou *et al.* (2014) examined the properties of RDF signifying the considerable effects that moisture, volatility and ash have on the fuels’ heating value.

A key limiting factor to this is the introduction and proportion of additional contaminants to RDF (e.g. chlorine from PVC, metallic catalysts), and due to their volatility, their retention within the alkaline clinker is extremely small (Bhatty, 2011). Where a high content of paper or cardboard products is residual to the MSW structure, this can also have a limiting effect on the thermal substitution capacity primarily due to large content of VM, ash and IM and the lower HHV (Becidan, 2007; Sørum, 2000).

Due to the heterogeneous and possibly hazardous nature of MSW, most cement plants do not co-incinerate unsorted waste as this could most likely result in degraded clinker quality or environmental outcomes (EC, 2003). As the most organic material is removed from recyclable and inert contaminants like glass, metal, or green waste; it is dried (to 25 wt.%), shredded and compacted into RDF pellets or bricks to a general density of about 0.7 tonne/m³ (IIP, 2014). Genon and Brizio (2008) notes that due to its man-made nature, comparatively RDF usually contains a low amount of carbon and sulfur, but higher amounts of chloride, moisture and heavy metals (particularly Sb, As, Cd, Co, Cr, Cu, Hg, Pb, and Zn) than that of carbonaceous fuels (Sørum, 2000).

In this mobile form, the transport, storage and handling of RDF is quite economic, however the quantity need for cement production can be of significance due to its generally low CV. The segregation of fuel from contaminates mentioned above allow for it to be further gasified if necessary. The supply of RDF into the kiln head (rather than inlet) or precalciner is through the plants normal equipment and handling facilities, however the kiln thermal and mass feed rates may need adjusting due to high dust content.
These potential changes can be less likely in the PC, it is of general preference for RDF to be used as secondary fuel replacement where combustion temperatures, O₂ and residence time, but this may have a variance to gas phase reactions. The supply of this to the PC is through a non-traditional open-belt weigh-feeder.

With expected emissions, the co-incineration of RDF has a relatively proportional CO₂ UMEF, with an EC report (2003) identified a potential global-warming reduction of 1.6 kg of CO₂eq/t of RDF (2.46) when compare to coal types (3.93). Similarly, the report also calculated a slight reduction in acidification (including hydrogen halides), nitrification and carcinogenic risk potentials from the combustion of RDF (5.96, 0.911, and 0.000034) in comparison to the combustion of coal (6.07, 0.938 and 0.000058), respectively. It was identified, however, of a precautionary 2 to 3-fold increase to baseline emission levels on Hg and Pb during the use of RDF.

A study by Mikulčić et al. (2013b) assessed the utilisation of RDF (comprising of 40 wt.% wood, textile and paper) in cement plants, with calculations showing that a 50 wt.% fuel substitution could achieve a high CO₂ UMEF reduction of 0.1044. Likewise, Rovira et al. (2010) investigated the RDF use at 20 ADF% (made-up with plastic (35 wt.%), paper (30 wt.%) and textiles (15 wt.%)) within a cement plant, finding similar emissions of PM, hydrogens and halides, heavy metals, and PCDD/Fs when compared to normal operations. This is of significance due to the high volatilisation potential of chlorides with recycled dust from the bypass gas in the PH where the formation of dioxins and PCBs are most likely to occur. For the use of RDF, no negative impacts to the plant process is identified, and effects to clinker include the possible transfer of fuel trace metals into the residual product.

Where RDF materials contain waste carpet, its energy value may be notably influenced if the constituents contain nylon or polypropylene shreds with a latex-rubber backing being at approximately 17 and 28 MJ/kg, respectively (Murray and Price, 2008). With a relatively high carbon-content, the potential for inert constituents of sulfur (from the rubber backing) or chlorine (from manufacture or its use) is most likely. Other pollutant-forming contaminants like magnesium or aluminium may exist in the filler, and fluorine or bromine is likely to exist as a flame-retardant application (Lemieux et al., 2004; Murray and Price, 2008).
A study by Lemieux et al. (2004) assessed the co-incineration of a shredded fibre fraction and a dust-like fraction directly into the rotary kiln, with fuel substitution rates of up to 30 ADF%. Compared to normal operations (RKIS), experimental trials showed no effects to PIC emissions (including CO, SVOCs and PAHs) and only a slight 5.3 vol% increase in NOx emissions due to the high presence of nitrogen in nylon. Lemieux et al (2004) showed that no statistically significant relationship existed between flue gas measurements and combustion conditions, as no evidence of rapid volatilization (and fuel-nitrogen NOx) and subsequent transient puff formations were observed.

Relative to the contribution ratio of PCDD to PCDF, several experiments (Altarawneh et al., 2009; Chen et al., 2014; Xhrouet et al., 2001) have co-incinerated RDF at the precalciner, showing the predominate contributions being from PCDFs, particularly relevant to the 2,3,4,7,8-PeCDF congener which accounted for up to 68% vol. of total I-TEQ UMEF. Conesa et al. (2008 and 2011) study on the release of acid gases (HCl, HF), metals, PAH and PCDD/Fs from the co-incineration of tyres and RDF (from municipal solids), showed dioxins to be considerably low (5 pg I-TEQ/Nm³) also with the most abundant congener being 2,3,4,7,8-PeCDF. These results also reported no correlation between dioxin emissions and ADF%. Rivera-Austrui et al. (2010 and 2011) performed continuous long-term monitoring of PCDD/F emissions beyond the EC (2000) Directive 2000/76/EC, showing that reliable and representative results are achieved during co-incineration and that multivariate analysis is a useful tool for data evaluation and identifying subtle differences amongst congeners.

Genon and Brizio (2008) highlights two key experiences in Italy with the co-incineration of RDF material in the precalciner, whereby fuel substitutions ranged between 7 and 24.5 wt.% with significant UMEF reductions to NOx (by 50 vol.%), SOx (by 40 vol.%), TVOC, CO (by 60 vol.%) and PM (by 75 wt.%). This is greatly relating to the sustained plant operating parameters and the fuel’s chemical composition, CV and ADF%. The differing kiln capacities of 79 tonnes per hour (t/hr) and 145 t/hr, respectively, were held to the standard operations for the kiln and precalciner (1.10-1.15 excess O2, >2 sec Kt) while the RDF composition was at CV= 18.84 MJ/kg, <10 H2O, <0.5 vol.% chlorine, and <5 ppmv PCB. With lower nitrogen values in RDF (0.3-0.7 vol.%) than that of coal (2 vol.%), the formation and emission of fuel NOx and SOx was reduced, while emissions were substantially higher for total and individual metals (not including Hg, Co, and Cu).
and PCDD/Fs. As the heterogeneity of RDF can differ from locations it can be hard to generalise the expected emissions, however the above results show to remained below regulatory required limits.

3.5.1.3 Plastics

A study by Al-Salem et al. (2010) showed plastics’ global production has tripled in recent decades to 260 million tonnes, with much of the household goods being composed of plastic or plastic reinforced materials, including packaging, clothing, general appliances and electronics. Plastic waste will be generated from households unless its properly segregated, it may also contain packaging, electronic and other waste materials. For the generation of waste within Australian industries, a significant 387,000 tonnes of plastic packaging (including polyethylene and PVC) and 444,000 tonnes of other plastics (polypropylene and polystyrene) were generated from manufacturing (at 53 wt.%), with a constant production rate of 400-500 kg/yr (Encycle Consulting, 2013).

With its relatively high CV, plastic is essentially the most readily available material for co-incineration however a stable and consistent composition may become problematic if it is to be continuously consolidated from differing sources. As there is limited published literature on the sole co-incineration of plastics alone, no current cement plant uses only plastic as a substituted fuel as it is entirely mixed with other waste streams predominately due to its very high chlorine composition and subsequent catalyst towards carcinogenic POPs (e.g. PAHs, PCDD/Fs, PCBs). The high chlorine content is consequentially due to the element being the key part of the polymer type, although it is necessary to still check the materials chemical composition for its co-incineration suitability and operational needs (Rahman et al., 2015). On the other hand, UNEP (2007) signify the use of waste plastics as a promising production fuel, particularly with its low immersed moisture content when compared to other alternatives like wood, paper, or biomass.

When compare to other petroleum-based waste products, polyethylene and polystyrene plastic can have the greatest effect in carbon offset (at 1.0 tonne CO₂/tonne coal) although this is counter-balanced when petcoke is used. Once shredded into manageable sizes, some facilities blend (with other products) and granulize the plastic to meet handling and combustion prerequisites, and inject it into the precalciner by pneumatic or mechanical means. The co-incineration of large particle plastic is avoided due to its volatile
combustion, which creates a reduced condition for clinker sinterisation (Twigger et al., 2001; Willitsch et al., 2003).

3.5.1.4 Waste tyres

Unusable vehicle tyres are sourced from various collection points and removed for their regulatory disposal, however Encycle Consulting (2013) identified a comparative 0.0004 wt.% (or 53,000 tonnes) of waste tyre/rubber is generated by Australian industries with only 25% being recovered for waste avoidance. As waste tyres have a relatively low ash and moisture content, the concentration of particulates and flyash formed through its use should be less than other fuel types. With the annual availability of almost 1 billion end-of-life tyres, the low diversity of material composition and high energy content (21-32 MJ/kg) makes it a consistent and effective fuel supplement.

Carrasco et al. (2002) examined co-incineration with TDF, showing a 15 wt.% increase to baseline TSP UMEF (289.8 to 252.9 mg/kg). With a comparatively low nitrogen content, there will less available to form NOx from combustion reactions, whereas the sulfur UMEF from tyres (1-2 wt.%) is dominant and similar to the 1-3 wt.% in most coals (excluding petroleum coke fuels). For these pollutants, Carrasco et al. (2002) showed a similar 11 wt.% reduction to baseline NOx UMEF (2.63 to 2.94 g/kg) and 23 wt.% increase to SOx UMEF (1.45 to 1.17 g/kg). These results when compared to other studies were shown to correspond to the fuel’s composition and combustion efficiency, which is also an important criterion to PIC formation.

With a high volatile matter (54-69 wt.%) and char content (23-30 wt.%), Larsen (2007) notes the occurrence of incomplete volatilisation (and generation of hydrocarbons or CO) is usually minimal due to the process high temperatures and long residence time. Subsequently, when hydrocarbon or CO levels were shown to be slightly higher than normal emissions, this is shown to be correlated with low PHgt and cycle times (Aranda-Usón et al., 2013; Chatziaras et al., 2016; IEA, 2010a). A study by Carrasco et al. (2002) showed a CO UMEF increase of 37 wt.% to baseline levels (356 to 261 mg/kg).

For heavy metals, most tyre makes do contain higher concentrations of Fe (12-15 wt.%) and Zn (up to 2 wt.%) in comparison to coal, of which can be encompassed into clinker along with PM and low concentrations of As and Ni (Evans and Evans, 2006; Larsen, 2007; Richards et al., 2008). Co-incineration tests by Carrasco et al. (2002) showed an
82 wt.% increase to total metal UMEF, with significant weight contributions of 487 wt.% being from zinc (2.36 to 0.4 mg/kg) due to being an important constituent of tyre make-up. Other elevated compound emissions included Cr at 340 wt.% more (0.45 to 0.1 mg/kg), Fe at 61 wt.%, and Al at 33 wt.. A decrease of 21 wt.% was shown for Hg and its compounds.

Even though the chemical composition of waste tyres can vary, they generally also contain chlorine, sodium, potassium and sulphur compounds which can catalyse and constitute additional air pollutants (e.g. PCDD/Fs, PCBs), kiln rings or preheater blockages (Evans and Evans, 2006; Twigger et al., 2001). Several studies have shown slight increased emissions with TDF, however a study by Carrasco et al. (2002) showed a decrease to PAH UMEF by 14 vol.% (124 to 143 μg/kg), and to PCDD/F I-TEQ UMEF by 45 vol.% (0.9 to 1.47 ng/kg).

Tyres fed into a precalciner are typically prepared by being chipped or shredded to a predetermined chip size which is manageable (generally 2 mm). The tyres’ inner steel reinforcement is not needed to be removed prior to preparation, as this will be heavily oxidised by the high operating temperatures during clinker production (Basel Convention, 2002). Material is conveyed into the precalciner so that its combustion is best supported by the chambers gravitational momentum (Twigger et al., 2001). As cement manufacturing has an alkaline environment, the co-incineration of waste tyres can reduce of NOx, SO2, TVOC and CO2 emissions while the residual of heavy metals being captured within the clinker material (Trezza and Scian, 2009). Pipilikaki et al. (2005) and examined the effects of clinker quality during a 6 ADF% co-incineration trial of TDF at the precalciner, and the results showed no creation of any undesirable compounds or that volatiles, zinc and total chromium was consistent with the use of coal.

Richards et al. (2008) provided a report of the air emissions data of 72% of cement plants (with a minimum of 4 large-diameter, in-line cyclones) permitted to co-combust whole and chipped tyres. The monitoring of numerous TDF and baseline emissions showed a 35% decrease to PM (0.029 versus 0.44 kg/t dry kiln feed) and NOx (443 versus 696 ppmv, standardised to 7 vol.% O2). Sulfur dioxide did however show similar emission levels, though there was some variability most likely due to plant variations.
From this publication, dioxin monitoring from 258 tests were standardised at 7 vol.% O₂, and identified the use of TDF resulted in ⅓ of the baseline emission level (at 99% statistical confidence) which were formed by a minimum of three tests under the use of coal. Of this data, the mean and median I-TEQ concentrations for total dioxins during TDF was at 0.021 and 0.004 ng/Sm³, respectively, indicating that the formation and release of several target pollutants either no effected or significantly reduced during the co-incineration of waste tyres.

As there is contrasting views (Batelle, 2002; Clauzade, 2006; ICF, 2008) on the combustion of TDF, this fuel source is of interest with similar studies (Giannopoulos et al., 2007b) showing no effects to the measured concentrations of PAH, BTX, PCDD/F and specific metals. As zinc is a generally high composition of tyres (1-2 wt.%), its residual concentration in fuel gas and ash material does apply some limitations to its sole use, with recommendations being that it remains below 30 ADF% (Pipilikaki et al., 2005; UNEP, 2011).

The USEPA (1997a) reviewed several laboratory and field tests with the use of TDF with a proximate and compositional analysis similar to the values in Table 3.2. Controlled laboratory tests examined the combustion of chunk (¼ of a tyre) and shredded (25 cm² pieces) for the emission of PM, CO, SO₂, NOₓ, TVOCs, metals, PAHs, PCDD/Fs and PCBs. The results showed a consistent, but slightly elevated EF on shredded material on most pollutants, and that semi-volatile organics had a similar, but lower mutagenic EF than particulate organics. Thirty field tests sourced the co-incineration of wire-free crumbed rubber (<0.64 cm) with natural gas at several steady-state combinations of fuel feed rate (0-24 ADF%), temperature and O₂ content. With the assessment to the above-mentioned pollutants, the USEPA (1997a) concluded that PIC is not formed through co-incineration, that potential emissions (except zinc) of TDF are comparatively similar to the combustion of carbonaceous fuels, and that kilns supplementing 10-20 ADF% (with existing APCDs) could still satisfy regulatory emission limits.

Greco et al. (2011) study of TDF co-incineration within 31 cement plants, identified PM reductions of 35% compared to baseline emissions, along with significantly lower values to NOx, most heavy metals and SO₂. While PCDD/F test results showed to be a third less than conventional fuels, reports have substantial increases to CO and TVOCs. CSI (2006)
and Karstensen et al. (2016) reviewed the international effects of PCDD/F emissions, concluding no relationship with these and the generation of POPs. Akkapeddi (2008) examined the co-incineration of tyres along with several other material mixes (including plastics and woodchips) but only with the analysis of certain gaseous pollutants (CO, NO$_x$, SO$_2$, TVOCs). The trials showed the plant could maintain the clinker composition and permeability to the four primary parameters (Al$_2$O$_3$, CaO, Fe$_2$O$_3$, and SiO$_2$) regardless of the selected fuels, along with UMEF values for CO (0.037 to 0.054), NO$_x$ (0.09-0.12), SO$_2$ (0.0009-0.0054), and TVOCs (0.0021-0.0034). When compared to baseline emissions, these represented reduced emissions with 1-10 ADF% tyres (NO$_x$ by 32%, SO$_2$ by 96%, TVOCs by 32%), with tyres and 12-22 ADF% plastics (NO$_x$ by 7%, SO$_2$ by 53%), and with 2.8-9.7 ADF% woodchips (SO$_2$ by 85%, TVOCs by 22%).

Zemba et al. (2011) database review of 132 individual tests further supports the CSI (2006) conclusion along with the co-incineration of wood, refuge derived fuel (RDF) and TDFs (average 26-30% weight basis), showing test results to be within regulatory limits for metals and PCDD/Fs. Furthermore, the IIP (2013) identify that due to its high CV value, up to 50% of thermal substitution with TDF in the precalciner would not result in any adverse clinker quality effects. As the use of ADF appears to be simply beneficial, the challenges associated with it must first be overcome (Madlool et al., 2011).

3.5.1.5 Bio-solids and sewage municipal sludge

Naturally, the production of sewage and its sludge is extensive in urbanised communities and can be a considerable concern for its management and limited disposal options (mainly by landfill, agricultural compost or energetic valorisation). The co-incineration of bio-solids or sewage sludge is recently introduced and currently accounts for 2 ADF% and offers a large CO$_2$ UMEF reduction and little environmental impact (Chatziaras et al., 2016; Zabaniotou and Theofilou, 2008). Typical calorific value of sewage sludge is reported to be at 16-17 MJ/kg but it is dependent on wastewater characteristics from which it is derived from. This plays a critical part to fuel substation as the volume of sewage sludge required to proportionally substitute a tonne of coal will range between 1.6 and 10.3 tonnes (Murray and Price, 2008; Twigger et al., 2001). With larger volumes, dried sludge is required to be effectively dried and mixed with conventional fuels so to reduce its nuisance odour and to minimise its danger of auto-ignition. Zabaniotou and
Theofilou (2008) highlight the ADF\% of sewage sludge should be controlled as experiments show increased NO\textsubscript{x} and SO\textsubscript{x} emissions with an increasing ADF\%.

As a carbon-neutral fuel, bio-solids and sewage sludge can also reduce NO\textsubscript{x} UMEF, however its concentration Hg is relatively high due to the cleaning process used in treatment plants. The application of sludge pellets can be either pneumatic or mechanically conveyed into the precalciner with an additional 3-4 vol.% of induced air (Kääntee et al., 2004; Twigger et al., 2001; Zabaniotou and Theofilou, 2008). This aids the removal of hydrogen halides (HCl, HF) and PCDD/Fs, thus minimising the possible clogging of pre-heater cyclones.

In addition to immersed moisture, other key considerations to co-incineration include the high ash content and the presence of volatile metals. As most metal compounds present in sewage sludge are captured in the clinker, the presence of its chlorine content can somewhat enhance volatilization of Cd, Hg and Pb (Aranda-Usón et al., 2013). A study by Zabaniotou and Theofilou (2008) showed the effective co-incineration of sewage sludge (with high H\textsubscript{2}O content) in Cyprus to have emission concentration of 0.7960 mg/Nm\textsuperscript{3} (for total metals) and 0.006 ng I-TEQ/Nm\textsuperscript{3} (for PCDD/F). The reduction of rapid Hg evaporation can be achieved if the raw meal has a high level of CaO and Cu. Studies by Rivera-Austrui et al. (2013 and 2014) showed a reduced concentration of 0.0033 ng I-TEQ/Nm\textsuperscript{3} (for PCDD/Fs) and 0.0009 ng TEQ/Nm\textsuperscript{3} (for dl-PCBs) during the co-incineration of a mixture containing RDF and sewage sludge.

Gálvez et al. (2007) studied the effects of raw meal to TVOC, PAH and PCDD/F compounds during the co-incineration of sewage sludge pellets, showing a slight reduction to most pollutants post-combustion. Volatile organics were shown to have no significant difference with the contact of the raw meal, whereas the heavier PAH compounds (> Chrysene) and most PCDD/F congeners have a beneficial decrease.

3.5.1.6 Spent carbon

Spent carbon dust is waste material sourced from electrolytic pot liners which convert alumina to aluminium, and is a suitable fuel and material replacement for combustion fuel and clinker material. As the global demand for aluminium increases its production, so does the generation of its waste by-products. The pot liners comprise of two distinct layers, namely a 55% conductive carbon layer and a 45% non-conductive insulation layer.
(CIF, 2005; Rahman et al., 2015), and the its fluoride content is shown to speed up the clinkering reaction which essentially reduces the necessary operating temperature (Herat, 1994; Kaddatz et al., 2013). Once broken up, the carbon layer can be useful as an alternative fuel source however its composition of leachable cyanide and some metals (Cr, Pb) can be a serious environmental concern and therefore requires further evaluation (Mikša et al., 2003).

As an effective source of fuel and materials, the co-incineration of pot liners in precalciners have grown more predominate in recent years and throughout many countries. Rahman et al. (2015) identifies the 99.9 vol.% DRE of inert cyanide when co-incinerated, along with the reduction of NOx and CO2 emissions when compared to baseline fuels. This reduction is primarily due to key operation conditions being maintained while other pollutants (such as hydrogen halides) are encompassed by the alkaline raw meal.

Trezza and Scian (2005) examined clinker quality effects during the co-incineration of pot liners, showing an increase in clinkering temperature, ash percentage and crystallisation, which subsequently effects the later milling capabilities. Despite the slight effects to the clinker mechanical properties, the results showed the use of this spent carbon waste as an energy substitute would still be suitable. A study by Kaddatz et al. (2013) further supports this with the inclusion that pot liners would reduce feed material volumes more than waste oils and TDFs.

3.5.1.7 Bio-hazard and hazardous waste

For several decades, biological and chemical hazardous waste has been processed within cement kilns (of up to 12% of alternative fuels) due to their environmentally-sound treatment options and predominately in those countries where legislative requirements permit for its co-utilisation (Murray and Price, 2008). The diversity of solid and liquid hazardous waste types is extensive, with the more commonly-found substances being pesticides, medical or pharmaceutical waste, solvents, oils, paints, resins, pesticides, oil, and lubricants.

Developing countries that currently lack the legislative approval or enforcement of co-incinerating hazardous waste, generally lack the awareness of proper waste segregation, handling, analysis and use. Karstensen et al. (2004b and 2005) supports this and identifies
the co-incineration investigation of a solvent-based aromatic insecticides during cement manufacturing in Vietnam. With intensive farming and limited waste management, pesticides were regarded as indispensable and therefore concoctions were needing its complete removal and destruction.

The selected insecticide contained two active ingredients, Fenobucarb (18.8 vol.%) and Fipronil (2.4 vol.%), with a necessary destruction and removal efficiency (DRE) of 99.99%. Results of the experimental burns showed no detection of the insecticide and that the DRE of PCDD / F, PCBs and Hexa-chlorobenzene (HCB) surpassed the above DRE requirement. Other results were shown to be like baseline emissions for TSP, CO, SOx, TVOCs, benzene, and heavy metals. Hydrogen chloride and hydrogen fluoride emissions were also shown to be acceptable even with the waste containing high concentrations of chlorine and fluorine.

3.5.1.8 Biomass

The main source of biomass is from agricultural crops, congealed organic waste or forestry residues, where its composition can vary and therefore its global use in the cement industry is limited to about 0.25% (Demirbas, 2003). The organic and energy content of biomass will vary dramatically from carbonaceous fuels and other waste types, with its physical properties containing less carbon, nitrogen, sulfur and chloride (than that of Anthracite), but more hydrogen, oxygen and volatiles. The conversion of biomass into thermal energy can be applied through combustion, gasification, pyrolysis, or the biochemical release of fermentation, anaerobic digestion and esterification. Depending on which state is used, the quantity of biomass to replace a tonne of coal will vary based on its energy value and moisture content. With this, the co-incineration of biomass residue could extend up to 20 ADF%, however, due to its unique and varied composition it is considerably difficult in large volumes to maintain process conditions (Saidur et al., 2011b). Process conditions which greatly influence each of these fuel states include flame ignition and stability, temperature, residence time, feed rate (for agglomeration), potassium and phosphorous salts, moisture content and particle sizing. This can lead to operating concerns with slagging or corrosion to the kiln (Demirbas, 2003; Murray and Price, 2008).
Saidur et al. (2011b) reviews several publications whereby the experimental combustion of biomass in boilers showed up to a 75 vol.% reduction of CO₂, NOₓ and SOₓ emissions, however PIC emissions (i.e. PM, CO) were significantly increased. As biomass produces a highly alkaline ash product, this aids the capture of CO₂ and SOₓ produced during its co-incineration with coal but can also decrease heat transfer within a cement kiln (Murray and Price, 2008). With biomass sourcing up to 14% of the world’s energy consumption (or 45,000 PJ-equivalent) (Saidur et al., 2011b), the World Business Council for Sustainable Development (WBCSD) identifies its global substituted use in 2009 was almost a third (2.9 wt.%) of the total 9.4 wt.% ADF%.

With this, the projected combustion of all non-carbonaceous fuels in kilns remains on target of 24 wt.%, with partial contributions from developed and developing regions. The achievement of this greatly depends on the cost of low-carbon fuel, the availability and compatibility of ADF, and the acceptance by governmental agencies (Greco et al., 2011; IEA, 2010a; WBCSD, 2010). However, with this objective, there must be an equal balance on the cause-and-effect of alternative fuel compositions and the compatibility of the cement manufacturing process. This is also consistent with alternative fuels of a liquid state.

3.5.2 Liquid

3.5.2.1 Paint residues and waste solvents

Paint thinners and solvent washings can be sourced as a by-product generated by chemical manufacturing or as an industrial waste, and is typically in a liquid pumpable state (Herat, 1994). Given its global generation and availability, it is being largely integrated into existing facilities for several decades, however its composition can vary greatly and is therefore difficult to generalise. Spent solvent is commonly shown to have a LHV of 25 MJ/kg, while paint residues can be sourced with a lower 20 MJ/kg heating value (Murray and Price, 2008). Of significance to these materials is the concentration of chlorine, necessary for specific reactions with heavy metals and sulfur for quality of clinker. For the application of paint residues and waste solvents, consideration may be required given its state, mixture and viscosity.

Previous solvent co-incineration investigations by Giannopoulos et al., (2007) showed a substantial 40 vol.% reduction in NOₓ emissions, however unburnt hydrocarbons and
particulates were shown to have increased. Murray and Price (2008) reported that while
the use of spent solvents should avoid CO₂ emissions, some tests have shown the use of
paint residue have had a slight increase to baseline emissions.

3.5.2.2 Waste oil

Waste oil is noted as a semi-liquid or liquid used product of which consists of mineral or
synthetic oils, oil-water mixtures or emulsions (EIPPCB, 2006). Inherently the co-
incineration of waste oils is of concern as it can contain traces of key pollutants, namely
heavy metals and PCBs. Generally classified as a hazardous material, its resource can be
from various points of origins including transportation, maritime vessels or structures,
agriculture or other industrial sources. Its availability throughout the world is extensive,
with about 1.1 million tonnes (half of which being treated for sediment separation) being
consumed each year for co-incineration in European cement plants (EC, 2003; EIPPCB,
2006; Murray and Price, 2008; Rahman et al., 2015). As liquid fuels do have the
advantage of producing large energy quantities per unit volume (17-38 MJ/kg), its co-
incineration will yield a higher inferred radiation which enhances radiant heat transfer to
the raw meal.

In comparison to crude-based heavy fuel oils, waste oil is heavily concentrated with heavy
metals, sulfur, phosphorus, and total halogens, however it will greatly depend on its
original source and use (Rahman et al., 2015). Some studies (Giannopoulos et al., 2007a
and 2007b; Herat, 1994), have shown the adoption of low-carbon waste fuels (including
oil, solvents and paints) can decrease the generation and release of PICs (particularly TSP
and CO), NOₓ, SOₓ, TVOCs, heavy metals, and PCDD/F emissions. Waste oil is
generally the more preferred ADF due to its VM content (~100 wt.%) and HHV (17-38
MJ/kg) when compared to solvents (18-23 MJ/kg). To address growing concerns on
changes to clinker quality from fuel substitution, Garcia et al. (2013) performed several
structural and engineering tests on clinker’s crystalline structure during waste oil co-
icineration, showing that no quality impacts were observed and all minimum
requirements were achieved.

Similar to solvents, the pre-treatment of waste oil is not necessarily required unless it has
been contaminated with sediment, water or other chemicals, or if it is required to be
blended with other viscous fuels to a desired composition for improved performance.
Separation can remove trace elements of As, Cd, Pb, BTX, PCDD/F and PAHs (Rahman et al., 2015). Karstensen et al. (2004b and 2005) undertook a survey on feasible ADF waste types in Vietnam alone, identifying up to 160,000 tonnes of an oil-based waste being readily available for use. Due to its hazardous nature, Karstensen et al. (2010) further examined the feasibility and destruction performance of PCB-containing oil in a rural cement plant of developing Sri Lanka, and to signify the capabilities of it as a combustion fuel substitute. The waste oil identified as Pyralene was sourced from electricity transformers where it is used due to its excellent heat-tolerating and non-mixing properties. With a composition of PCB (59%), trichlorobenzene (36%) and tetrachlorobenzene (5%), the material is non-degradable and possesses terrible malignant characteristics.

Mixed homogenously with diesel-washings, this was applied under two ADFfr (equivalent of 7 and 10.05 kg PCB per hour) while achieving DRE rates of 99.999944% and >99.999999%, respectively. These results showed it to be a comparatively-sound treatment and disposal with the complete destruction of the waste oil without the emission of newly-formed PCDD/F, PCB or HCB compounds. If newly-formed pollutants were generated, the passing of these through the preheater zones would absorb components of it into the fine raw material. Emissions monitoring for other pollutants (i.e. TSP, CO, SOx, TVOCs, benzene, HCl, heavy metals, and PAHs) were shown to be like normal operations or below laboratory detection.

3.5.3 **Disadvantages of using alternative fuels for heat and energy**

Industries involved in the co-incineration of hazardous or waste materials can inherently be of concern as they are likely to contain or generate key air pollutants. Where industries gradually continue to substitute waste for its combustion and calcination needs, published literature needs to be reviewed and gap identified so that small-scaled experimental trials can be performed within regulatory guidelines, and in-situ emissions monitoring conducted and published during its final co-incineration process. The selection and use of co-incinerating fuels should also incorporate logistical measures of handling, preparation, conditioning, storage, dosage, feeding and operational (burning) influences (Willitsch et al., 2003).
However, caution must prevail as the differing physical and chemical properties of alternative fuels can consequentially diminish key fuel-combustion conditions, generate incomplete combustion and give preference to one substance (e.g. PCBs) over another (e.g. PAHs). Studies by Conesa et al. (2008) and Alsop (2014) have also shown fuel variations can alter the stoichiometric ratio of alkalis (at 1.5%), resulting in a higher risk of shell corrosion to the kiln, precalciner circulation blockages or pollutant-forming catalysts (e.g. inorganic volatiles, HCl, or temperature).

This is predominately due to the mass unit formation and emission of pollutants are of concern as they are contingent to the plants’ configuration, suppression capability, fuels and materials used, and post-combustion control devices (Andronescu and Puscasu, 2012; Karstensen, 2014b; Zemba et al., 2011). Therefore, the planning and undertaking of waste utilisation in cement manufacturing needs to be completely investigated and communicated. This extends into an open-dialogue engagement about ADF proposals with external stakeholders, regulatory agencies and neighbouring communities.
Chapter 4: Research Methodology and Design

For this thesis, the quantitative measurement of operating and emission parameters and the testing of empirical hypothesis will support answers to the research questions (Newman, 2003) while determining the degree of association between the parameters. This chapter details the research methodology and design used, including those used during field monitoring and laboratory analysis.

4.1 Research design

The experimental design for this research involves the analytical testing of flue gas from 10 cement batching plants (referenced A, B, C up to J) of various production capacities and which have been operating over several years. The average annual clinker production for each plant is approximately:

- Plant A – 0.65 mtpa
- Plant B – 0.53 mtpa
- Plant C – 0.51 mtpa
- Plant D – 0.94 mtpa
- Plant E – 1.3 mtpa
- Plant F – 0.53 mtpa
- Plant G – 0.48 mtpa
- Plant H – 0.26 mtpa
- Plant I – 0.85 mtpa
- Plant J – 1.6 mtpa

The cement plants were selected while they were actively operating with conventional fuels (collected as baseline emissions) or with the partial substitution of low-carbon ADF only at the precalciner secondary fuel location (collected as experimental emissions). The plants were identified with varying kiln dynamics and an initial feasibility study identified if they were adequately designed, equipped and able to conduct the experimental tests while potentially able to respond (if necessary) so to remain in compliance with government imposed license limits. Process parameters under normal operations is used to monitor if a process upset was to occur, so that necessary controls could be applied and the representativeness of experimental trials would not be affected. The utilisation of real-world batching plants was selected over laboratory tests whereby process controls and influences would not be compromised and the results are therefore representative.

For experimental tests, the quantity of ADF% and its fuel firing rate (PCₖₑ) were calculated by the calorific substitution of the secondary fuel so to minimise the impact to the plants’
natural process, clinker quality, and for later comparison to baseline emissions. While all emissions testing was conducted over different days, the plants’ operating conditions (including meal feed rate) and emissions were held close to normal as reasonably possible. Variations in maintaining certain parameters (e.g. temperature, residence time, $S_1$) were expected due to the natural fluctuations of the process and its magnitude. Subsequently, as the consequential effects on the clinker quality assurance and its inherent cost may be somewhat imposed by standardising experiment parameters, this influence is globally recognised as acceptable due to the underlying objectives.

For baseline emissions monitoring, a minimum of 3 runs were conducted on the stack sampling ports of each rotary kiln, with consecutive sample numbering of these being done for each plant, such as A1, A2, A3 through to A8 for cement plant A. The target analytes for each run included those identified in subchapter 2.6. With the timing for process stability and the number of stack samples required for each run taking several days, process parameters were recorded and if no inconsistencies were present then the systems’ operating condition is the average of the sampling duration. During the undertaking of each sample run, conditions of the following plant operating parameters were recorded:

- Kiln and PC fuel type, CV (MJ/kg) and firing rate (t/hr);
- ADF type, ADF$\%$ and PC$_{fr}$ (t/hr);
- Mass flow (t/hr) of meal feed and clinker load;
- Kiln flame temperature (°C) and residence time (s);
- Clinker exit temperature (°C);
- gas temperature (°C), material temperature (°C), and material residence time (s) within the PH cyclones, PC vessel or kiln chamber;
- rate of induced air (m$^3$/hr), corresponding $S_1$ and excess air (%);
- total energy consumed per clinker tonne (GJ/tonne); and
- Flue gas temperature (°C), velocity (m/s), H$_2$O content (vol.%), and O$_2$ / CO$_2$ concentrations (vol.%).
4.1.1 **Material selection**

Experimental run simulations were conducted to the respective plants’ baseline runs, with all fuels being thoroughly mixed prior to use. A total of 94 baseline and experimental runs were sampled and monitored. The selection of ADF was based on previously published investigations (as discussed in subchapter 3.5), readily available and marketable materials, or alternative waste products near the receiving facility. With some fuel types (e.g. wood, plastics, activated carbon) intended to be co-incinerated over several years and at various cement plants, its consistent preparation for use and transportation remained a prerequisite. The low-carbon fuels were selected to proportionally substitute a specific calorific supply of petroleum coal, and included:

- waste oils made from a 1:1 mix of cutting fluids and vehicular engine oil (at 3.5, 5, 5.5 and 7.5 ADF%);
- pascalco sand mixed with about 12 wt.% petcoke (at 15 ADF%);
- wood chips (at 7, 10 and 25 ADF%);
- RDF comprising of wood chips and 5-10 wt.% plastics (at 40 ADF%);
- spent carbon dust from alumina smelter anode formers (at 10 ADF%);
- waste solvents residue from cleaning and painting operations (at 7 ADF%); and
- shredded vehicular tyres (at 5.5, 7.6, 8.1, 14 and 19 ADF%).

4.1.2 **Material composition and preparation**

The general composition of the above ADF, its relevant CV (above 550°C) and percentage of plant fuel substitution are shown in Table 4.1 and discussed further below. Additional information on the raw meal composition was collected during each run, however its screening showed absolute a minor statistical variation amongst samples and between facilities, despite being in separate locations.

In preparation of each cement plant’s consecutive fuel sample, an ongoing assessment was performed on the previous sample’s chemical and physical composition, fuel suitability (due to catalytic and trace pollutants) for maintaining compliance, and the acceptability to increase the percentage of ADF substitution. In the event of an unacceptable inconsistent between sample composition and CV, this fuel product would not be used for the experimental trials.
The collection of used cutting fluids from steel manufacturing and used vehicular engine oil allowed for an average ADF composite of 1:1. With an unusually high viscosity, maintaining a long-term uniform mix of these oils was shown to be somewhat problematic with stratification. Furthermore, characterisation of the mix showed a relatively low HHV of 30 MJ/kg. Material logistics between and within cement plants was shown to be relatively seamless, with a stable homogenous supply of fuel being mixed with the powderised coal at the precalciner double-gated chute through a pneumatic line and nozzle. Wood materials used were a mixed-source of construction, timber mill, and residential demolition wastes. These were initially dried prior to chipping to particle lengths of 25-35 mm, with wood chips composites showed a similar low HHV of 18 MJ/kg to other reported values shown in Table 3.2.

### Table 4.1: Summary of ADF characteristics for experimental tests.

<table>
<thead>
<tr>
<th>ADF type</th>
<th>Proximate &amp; composition analysis [wt.%, dry]</th>
<th>CV [MJ/kg]</th>
<th>Sample reference</th>
<th>ADF %</th>
<th>Equivalent replacement (tpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste Oil</td>
<td>17-30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pasminco sand</td>
<td>25-27</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood chips</td>
<td>14-18</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood chips &amp; 5-10% plastics</td>
<td>26-27</td>
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<td></td>
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<tr>
<td>Carbon dust</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waste solvents</td>
<td>18-21</td>
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<tr>
<td>TDF</td>
<td>24-30</td>
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### Table 3.2: Summary of ADF characteristics for experimental tests.

<table>
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<tr>
<th>Sample reference</th>
<th>ADF %</th>
<th>Equivalent replacement (tpa)</th>
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<tr>
<td>A4</td>
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</table>

100
The RDF material sourced was from an off-site waste sorting facility which supplied pulverized wood pieces blended with dried shredded plastic (gravimetrically mixed at 5-10 wt.%) to a mean particle length of 12-15 mm. This size was selected so to reduce the opportunity of fuel blockages and to assist with fast burning. With a low-carbon composition (45-70%), the calorific estimation for the RDF used was relatively high at 27 MJ/kg when compared to other literature (Bhatty, 2011; Genon and Brizio, 2008; Rovira et al., 2010) RDF calorific values of 20 MJ/kg, most likely due differences in plastic material sourced from industrial or residentially. In this mobile form, both wood and RDF materials were sustainably mixed with coal at the prescribed quantities, and supplied to the precalciner through a non-traditional open-belt weigh-feeder. Pasminco sand was sourced as an industry by-product waste which had been inadvertently mixed with approximately 12 wt.% petroleum coke, and spent anode pot liners sourced where transported from a nearby aluminium smelter. For the use of pasminco sand and the anode-carbon dust (conductive and non-conductive layers inclusive), the preparation of these were similar to pulverized coal, and was supplied to the precalciner through the plants normal equipment and handling facilities.

Approximately 12,000 litres (stored in 204-litre drums) of a highly-viscose solvent residue from spent cleaning and painting operations was sourced from 3 facilities. The two active ingredients of the solvent were analysed at 10.1% naphthalene and 6.3% methyl ethyl ketone, with small heavy metal composites from marine paints (mainly consisting of Be, Cd, Ni and Zn). The material was shown to have a relatively low maximum CV of 21 MJ/kg. Unusable vehicle tyres were sourced from a collection point, which were shredded into approximately 25 mm squares, with an average CV of 30 MJ/kg and sulfur content of 1 wt.%. The TDF was transported between 2 cement plants, both of which feed the material into the precalciner double-gated chute by bucket elevators.

4.2 Sampling and Analytical Methodology

Sampling of pyro-processing flue gas aids to detect and determine the presence of pollutants and its UMEF, to evaluate if the emissions are within its regulatory limits, and to display the efficiency and effectiveness of the chosen APCD. Flue gas monitoring also sets a benchmark which allows for improvements in existing processes, or aids the development of new and advancing processes. As standardised techniques used for the
monitoring of real-world cement plants are a frequent requirement by regulatory bodies, the sampling and analytical methods were specifically selected and performed in accordance with these techniques. The monitoring of the flue gas pollutants is to provide:

- a replicate gas sample containing the same amount of pollutant,
- the conditioning of the sample to moisture, temperature, and O$_2$ (or CO$_2$),
- the separation and measurement of desired pollutants from the air sample, and
- measuring of sample flow rate and isokinecty (Wight, 1994).

The analytes of interest to this research include:

- by dry continuous sampling: oxygen$^{16}$, carbon monoxide$^{16}$, carbon dioxide$^{16}$, nitrogen oxides$^{16}$, and sulfur dioxide$^{16}$.
- by wet sampling: total solid particulate (TSP) matter$^{17}$, sulfur dioxide$^{17}$, sulfur trioxide$^{17}$, halides and halogens$^{17}$, heavy metals$^{17}$, volatile organic compounds$^{16}$, polycyclic aromatic hydrocarbons$^{17}$, polychlorinated dibenzo –p dioxins and furans$^{17}$, and polychlorinated biphenyls$^{17}$.

Sampling access to the process flue gas was via four 6” flanged ports located at the emission stack’s point source (seen in Figure 2.4). The methods used for the assessment of the flue gas conditions for isokinetic sampling is firstly discussed.

4.2.1 Stack traverse points

The traverse points within the stack cross-section was determined in accordance with USEPA Method 1 – ‘Sample and Velocity Traverses for Stationary Sources’ (USEPA, 1983a). This method selects the minimum number and location of equal areas along the circular cross-sectional plane perpendicular to the gas flow direction, based on the extent of nearby flow disturbances (Wight, 1994). Flow disturbances can be an upstream or downstream feature which produces a variation in the gas velocity and direction across the sampling plane. To correct this, the traverse points are identified within each of the equal areas and the and the sample velocity is slightly altered, gaining a more representative measurement of pollutant UMEF.

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$^{16}$ Non-Isokinetic sampling

$^{17}$ Isokinetic sampling
4.2.2 **Stack gas velocity and volume flow rate**

The stack gas velocity and volumetric flow rate used on each sample was determined in accordance to USEPA Method 2 – *‘Determination of Stack Gas Velocity and Volume Flowrate (type s pitot tube)’* (USEPA, 1983b). The average test velocity was determined from the gas molecular weight and the measurement of velocity head at each traverse point, by using a Stausseheibe (s-type) pitot and a differential pressure gauge (i.e. manometer). **Figure 4.1** shows the vital positioning of the s-type pitot tube (with a calculated 0.84 co-efficient), thermocouple, and sampling nozzle in a local vicinity, and being parallel to the gas flow direction. The volume flowrate at each traverse point was calculated with the stack cross-sectional area and its velocity. The estimated measurement of uncertainty\(^\text{18}\) for gas velocity and flow rate measurements was within ± 5 vol.%.  

![Figure 4.1: Sampling nozzle and S-type pitot tube showing impact and static pressures](Source: ISO, 1994; USEPA, 1983b)

4.2.3 **Gas temperature**

The temperature of the flue gas was measured in accordance with British Standards 1041 Part 4 – *‘Guide to Selection and Use of Thermocouples’* (BSI, 1992). The alignment of the temperature sensor, s-type pitot, and sampling probe as per **Figure 4.1** ensured...

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\(^{18}\) Based on ISO 20988:2007 standard
accurate stack gas temperature readings at each traverse point. The estimated measurement of uncertainty\textsuperscript{18} for this method was within ±5%.

4.2.4 Moisture content (water vapour)

The determination of the stack moisture content was conducted in accordance to the USEPA Method 4 – ‘Determination of Moisture Content in Stack Gases’ (USEPA, 1983c). A measured volume of flue gas was isokinetically drawn through a heated quartz-glass nozzle and probe line, condensed through a series of chilled Greenberg-Smith impingers (each containing 100 mm of water), and through a final impinger of silica gel. The total change in water volume and silica gel weight was used to calculate the percentage moisture in the gas. The estimated measurement of uncertainty\textsuperscript{18} for this method was within ±5 vol.\%.

4.2.5 Dry and total molecular weight

The dry molecular weight of stack gases was determined in accordance with USEPA Method 3 – ‘Gas Analysis for the Determination of Dry Molecular Weight’ (USEPA, 1990). The gas sample was withdrawn from the source stack, and conditioned with the removal of moisture and PM. The conditioned gas was then analysed for CO\textsubscript{2}, O\textsubscript{2}, CO and N\textsubscript{2} (by dry continuous sampling, subchapter 4.2.7) and the dry molecular weight was determined from the percentage of each compound. The addition of the water vapour fraction was used so to determine the total molecular weight.

4.2.6 Isokinetic sampling

Source gas was withdrawn isokinetically through the nozzle of a clean multicomponent sampling train to ensure an accurate and defensible sample of the aerosols and particulates, regardless of particle size or inertia (Wight, 1994). Isokinetic sampling for several test methods effectively require for the sharp-tapered nozzle to be parallel with the carrier gas flow direction along numerous traverse points, so that the sample velocity at the nozzle inlet was altered to mirror the approaching stack gas velocity and any nearby flow disturbances (as seen in Figure 4.2).
Figure 4.2: Isokinetic sampling from exhaust gas to nozzle inlet (Baukal, 2004).

Over the duration of the sampling, changes in the isokinetic flowrate at the traverse point was done to create variation in the samples’ true representation. The sample’s percent isokinetic (%I) was calculated post-test (to within 100 %I ± 10%), signifying the samples accuracy and validation of the carrier gas due to variations at each traverse point. Once sampled, the results of the flue gas measurements were used to calculate the normalised flow rate at 0 °C temperature (273 K) and 1 atmospheric pressure (101.325 kPa), and the standardised flow rate at 10 vol.% O\textsubscript{2} (dry gas) reference. The UMEF (in kg/tonne) was calculated on each pollutant’s mass emission rate per unit of clinker produced.

4.2.7 Continuous methods

4.2.7.1 Oxygen and carbon dioxide

Oxygen and carbon dioxide concentrations are monitored in accordance with USEPA Method 3A - *Determination of Oxygen and Carbon Dioxide Concentrations in Emissions from Stationary Sources (Instrumental Analyser Procedure)* (USEPA, 2006). In accordance with this method the sample gas was withdrawn continuously from the gas stream and portions were conveyed to an instrumental paramagnetic O\textsubscript{2} analyser (serial 01133471) and a Non Dispersive Infrared (NDIR) CO\textsubscript{2} analyser (serial 01008558). A Testo 350XL portable multi-gas emissions analyser (Myers et al., 2003), calibrated to National Association of Testing Authority (NATA) certified O\textsubscript{2} and CO\textsubscript{2} span gases and zeroed with UHP nitrogen, was used as this instrument. The system was fitted with an
out-of-stack filter and condenser, and was operated to the 0-25 vol.% O$_2$ range and the 0-50 vol.% CO$_2$ range. The UMEF for CO$_2$ was calculated from the results, with an estimated measurement of uncertainty\textsuperscript{18} for this method was $\pm 2$ vol.\%.

4.2.7.2 Carbon monoxide

Carbon monoxide concentrations are to be monitored in accordance with USEPA Method 10 - *Determination of Carbon Monoxide Emissions from Stationary Sources (Instrumental Analyser Procedure)* (USEPA, 2008a). In accordance with this method the sample gas was withdrawn continuously from the gas stream and conveyed to a NDIR CO analyser (serial 01025427) whereby a moving membrane measures the difference in radiation that is passed through the cell. A Testo 350XL portable multi-gas emissions analyser (Myers *et al*., 2003), calibrated to a NATA certified CO gas and zeroed with UHP nitrogen, was used. The system was fitted with an out-of-stack filter and condenser, and was operating with a 0-10,000 ppmv CO range. The UMEF for CO was calculated from the sampling results, with an estimated measurement of uncertainty\textsuperscript{18} for this method was within $\pm 3$ vol.\%.

4.2.7.3 Nitrogen oxides

Nitric oxide and nitrogen dioxide concentrations is monitored in accordance with USEPA Method 7E - *Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyser Procedure)* (USEPA, 1986a). In accordance with this method the sample gas was withdrawn continuously from the gas stream and a portion was conveyed to a NO/NO$_2$/NO$_x$ Chemiluminescent analyser (serial 01138341). A Testo 350XL portable multi-gas emissions analyser (Myers *et al*., 2003), calibrated to NATA certified NO and NO$_2$ span gases and zeroed with UHP nitrogen, was used. The analyser uses a stainless steel catalytic converter for the reduction (and later detection) of NO$_2$ to NO, and the total nitrogen oxides are expressed as NO$_2$. The system is fitted with an out-of-stack filter and condenser, and was operating with a 0-4,000 ppmv NO range and a 0-500 ppmv NO$_2$ range. The UMEF for NO$_x$ was calculated from the results, with an estimated measurement of uncertainty\textsuperscript{18} for this method was within $\pm 3$ vol.\%.
4.2.7.4  **Sulfur dioxide (dry method)**

Sulfur dioxide concentrations are monitored in accordance with USEPA Method 6C - *Determination of Sulfur Dioxide Emissions from Stationary Sources (Instrumental Analyser Procedure)* (USEPA, 2008b). In accordance with this method the sample gas was withdrawn from the gas stream and conveyed to a NDIR SO$_2$ analyser. A Testo 350XL portable multi-gas emissions analyser (Myers *et al.*, 2003), calibrated to NATA certified SO$_2$ span gases and zeroed with UHP nitrogen, was used. The system was fitted with an out-of-stack filter and condenser, and was operating with a 0-5,000 ppmv SO$_2$ range. The UMEF for SO$_x$ was calculated from the sampling results, with an estimated measurement of uncertainty$^{18}$ for this method was within ± 5 vol.%.

4.2.8  **Particulate matter**

4.2.8.1  **TSP and USEPA sampling train**

Sampling for TSP was conducted in accordance with USEPA Method 5 (AS4323.2-1995) – *Determination of Particulate Matter Emissions from Stationary Sources*’ (USEPA, 1987b). The USEPA Method 5 multicomponent sampling train (Figure 4.3 and Figure 4.4) is the most widely used and required technique for flue gas monitoring on high temperature combustion processes, and consists of the following components leading from the flue gas: nozzle (1), heated quartz-glass probe (2), hot box with heated particulate filter (3), condenser and reagent Greenburg Smith impingers (4), diaphragm pump (5), gas meter (6), and manometer / thermometer (7).
For this and other isokinetic methodologies, once the relevant sampling train was assembled, a pre-test leak check was performed whereby the diaphragm pump was started.
and a leak-tight stopper was applied to the nozzle inlet. After a check on the manometer for any evidence of air flowrate leaks, the stopper (and vacuum) was slowly removed.

After a pre-test leak check, the flue gas was isokinetically pulled through the nozzle and temperature controlled glass-lined probe. Particulate matter is collected on a pre-weighed glass fibre filter (GFF) located within a heated glass filter holder and frit, housed within the hot box. The heated probe and hot box was regulated to maintain a constant temperature of 120 °C ±10 °C (to sufficiently prevent condensation). The efficiency of the filters selected and used was to the ASTM Standard Method D 2986-71, to capture 99.95 wt.% of particulates sized to 0.3 µm.

From the hot box, the gas continued down through to a series of four Greenberg-Smith impingers each containing 100 millilitres of chilled water (to approximately 14 °C) for condensing, and through a final impinger of silica gel. The sample gas was pulled through the equipment by a vacuum pump, and through a calibrated dry gas meter for the measuring of gas temperature and volume. A leak check was performed at the change of sampling ports and at the end of the sampling period. The weight change of the pre-weighed GFF was determined with a certified balance, and used to calculate the concentration, emission rate and UMEF for TSP. The estimated measurement of uncertainty for this method was within ± 10 wt.%.

4.2.8.2 **PM$_{10}$ and PM$_{2.5}$ particulate matter**

Monitoring for PM$_{10}$ and PM$_{2.5}$ particulate matter was conducted in accordance with USEPA Method 201A - ‘*Determination of PM$_{10}$ and PM$_{2.5}$ Emissions from Stationary Sources (Constant Sampling Rate Procedures)*’ (USEPA, 1997b). In accordance with this method, a sample of stack gas was extracted at a predetermined constant flow rate through a combined cyclone sampling head. This in-stack sizing device separated particles with nominal aerodynamic diameters (of 10 µm and 2.5 µm) by centrifusion. To minimise variations in the isokinetic sampling conditions, testing was conducted within well-defined limits. Gases were then conditioned (for removal of moisture) and finally metered for flow rate and sample volume. The particulate mass for each size fraction was determined by gravimetric analysis. The UMEF for PM$_{10}$ and PM$_{2.5}$ was calculated from the sampling results, with an estimated measurement of uncertainty for this method was within ± 15 wt.%. 

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4.2.9 **Sulfur dioxide and sulfur trioxide (wet method)**

Testing for $H_2SO_4$ (including $H_2SO_4$ mist), $SO_3$ and $SO_2$ was performed in accordance with USEPA Method 8 - ‘Determination of Sulfuric Acid and Sulfur Dioxide Emissions from Stationary Sources’ (USEPA, 1977). A measured volume of stack gas was withdrawn isokinetically from the stack through a series of four Greenburg Smith impingers, with the first and second impingers being separated by a 47 mm GFF housing. The first impinger contained an aqueous solution of 80 vol.% isopropanol (IPA), used to remove $H_2SO_4$ and $SO_3$ from the gas stream. The second and third impingers each contained an aqueous solution of 3 vol.% hydrogen peroxide ($H_2O_2$) for the collection of $SO_2$, with the final impinger being empty to collect any carry-over solution. After sampling, the concentration fractions of $H_2SO_4 / SO_3$ (from the aliquot IPA solution and GFF) and $SO_2$ (from the $H_2O_2$ solution) was determined separately at a laboratory through the standards’ barium-thorin titration method. The UMEF for $SO_x$ was calculated from the sampling results, with an estimated measurement of uncertainty for this method was within $\pm 10$ vol.%. 

4.2.10 **Hydrogen halides and halogens**

Source monitoring for chloride, chlorine, fluoride and fluorine was performed in accordance with USEPA Method 26A – ‘Determination of Hydrogen Halide and Halogen Emissions from Stationary Sources – Isokinetic Method’ (USEPA, 1994a). Particulate pollutants were withdrawn isokinetically from the source gas, through a heated quartz-glass nozzle and Teflon-lined probe, and collected on a heated GFF. Gaseous pollutants that passed through the GFF were condensed into two Greenburg Smith impingers of 0.1 mol $H_2SO_4$ and two Greenburg Smith impingers of 0.1 mol sodium hydroxide (NaOH). Sodium thiosulphate (25 mg) was added to the NaOH solution post-sampling, to assure complete reaction with each available halogen molecule.

The filter collected particulate matter (including halide salts) was discarded and not used for laboratory analysis. The hydrogen halides were solubilised in the $H_2SO_4$ solution by forming chloride and fluoride ions. As the halogens have a very low solubility, they passed through the $H_2SO_4$ solution and were later hydrolysed in the NaOH solution. The halide ions and halogens were each solubilised, and later laboratory measured from each aqueous solution by the standards’ ion chromatography method, and the acid gases later
expressed as HCl and HF. The UMEF was calculated with an overall estimated measurement of uncertainty\textsuperscript{18} for this method was within ± 15 vol.\%.

### 4.2.11 Heavy metals

Monitoring for heavy metals and their compounds was performed in accordance with USEPA Method 29 - ‘Determination of Metal Emissions from Stationary Sources’ (USEPA, 1999). A representative sample of flue gas was withdrawn isokinetically through a heated quartz-glass nozzle and probe liner, with PM being collected on the internals glass surfaces and on a heated quartz fibre filter (QFF). Gaseous metal pollutants that passed through the QFF were condensed and collected downstream into two Greenburg Smith impingers containing an aqueous acidic solution of hydrogen peroxide (5 vol.% HNO\textsubscript{3} and 10 vol.% H\textsubscript{2}O\textsubscript{2}), and two Greenburg Smith impingers containing an aqueous acidic solution of potassium permanganate (10 vol.% H\textsubscript{2}SO\textsubscript{4} and 4 vol.% KMnO\textsubscript{4}). At the end of each run, the sampling train was disassembled and washed with 0.1 mol HNO\textsubscript{3} solution.

Samples were recovered from the probe, filter, and aqueous acidic solution of H\textsubscript{2}O\textsubscript{2} for the later laboratory analysis of Sb; As; Ba; Be; Cd; Cr\textsuperscript{3+}; Cr\textsuperscript{6+}; Cu; Fe\textsubscript{2}O\textsubscript{3}; Pb; Mn; Hg; Ni; and Zn compounds, and the appropriate fractions were determined by inductively coupled argon plasma - mass spectrometry per USEPA SW-846 Method 6020 (USEPA, 2007a). The aqueous acidic solution of KMnO\textsubscript{4} was analysed only for Hg, and was determined by cold vapour atomic absorption spectroscopy per USEPA SW-846 Method 7470a (USEPA, 1994b). The estimated measurement of uncertainty\textsuperscript{18} for this method was within ± 10 wt.\%.

### 4.2.12 Total volatile organic compounds (TVOCs)

Sampling and analysis for TVOCs was performed in accordance with USEPA Method 18 – ‘Measurement of Gaseous Organic Compound Emissions by Gas Chromatography – Adsorption tube procedure’ (USEPA, 1994c). A measured volume of stack gas was drawn through a series of chilled, midget Teflon impingers (for condensate) and then an activated carbon (charcoal) absorption tube, trapping the organic vapours which were present in the gas. Samples were extracted from the carbon tube with carbon disulphide and analysed (with the condensate) using a gas chromatograph coupled to a flame
ionisation detector. The total response was then measured relative to an n-hexane standard. The measurement of uncertainty for this method was $\pm 10$ vol.\%.

### 4.2.13 Semi-volatile organic compounds, including PAHs

Sampling for semi-volatile organic compounds (SVOCs), including PAHs, was conducted in accordance with USEPA SW-846 Method 0010 – ‘Modified Method 5 Sampling Train’ (USEPA, 1986c) as seen in Figure 4.5. Stack gas was extracted isokinetically through a heated quartz-glass nozzle and probe liner, and a 120 °C hot box (containing a high-efficiency GFF) for the collection of organic-laden particulate materials. The stack gas was then intensely chilled (to approximately 14 °C) through recirculating ice-water coolant (in the outer jacket) before passing through a chilled XAD-2 sorbent cartridge (sustained at <50 °C).

![Figure 4.5: USEPA Modified Method 5 Sampling Train for SVOC, PAH, PCDD/F, and PCBs (Source: USEPA, 1986b).](image)

The XAD-2 resin is a hydrophobic bed of porous polymeric adsorbent made from porous polystyrene co-polymer beads, and forms a mesh-style bed to absorb soluble organic compounds from aqueous streams and organic solvents. The XAD-2 resin was spiked with a range of isotopically labelled PAH surrogate standards prior to sampling, and was used to collect targeted semi-volatile organic species that pass through the GFF in the gas.
phase. Semi-volatile species are defined as compounds with boiling points >100 °C. A condensate knockout trap and series of Greenburg Smith impingers were located immediately after the sorbent cartridge. At the end of each run, the sampling train was disassembled and washed with toluene and acetone solutions. The GFF and resin cartridge was wrapped with foil during transportation to the Australian Government’s National Measurement Institute (NMI) laboratory.

In the laboratory, recovery standards were added to the sample components. The filter, resin column, impinger condensate solution and washings were spiked with isotopically-labelled PAHs and extracted with organic solvents. The laboratory determination and concentration of SVOCs was performed by a Hewlett-Packard 5972 gas chromatography-mass spectrometry with a DB-5ms column (30m x 0.25mm x 0.25 µm) in accordance with USEPA SW-846 Method 8270c (USEPA, 1996).

The percentage recovery for labelled PAH surrogate standard was assessed used to measure the concentration of native PAHs and surrogates, to indicate how effective the sample train resin was in retaining the collected PAHs (lab surrogate recovery, R*) and to measure the effects caused by time, storage and transportation (field surrogate recovery, Rf). Laboratory results included the correction for the internal standard recoveries. Where surrogate recoveries do not meet the USEPA (1986c) permissible range of 50 to 150%, sample runs will be considered unreliable (possible due to resin breakthrough or cross-contamination) and therefore excluded from the data set.

From the chemical analysis, the USEPA Priority Pollutant PAH total TEQ was calculated using toxic equivalency factors (TEF) based on benzo(α)pyrene (BaP) as specified in the WHO Environmental Health Criteria 202 (WHO, 1998), shown in Table 4.2. Sampling characteristics father standardised the UMEF for SVOC and PAH priority pollutants, and BaP-TEQ PAHs (WHO basis) were calculated (with and without) analytical instruments limit of detection (LOD) values. The standardisation of these compounds is referenced within this thesis as PAH BaP in or PAH BaP ex, respectively. The estimated measurement of uncertainty for these methods was within ± 10 wt. %.
Table 4.2: PAH BaP-TEQ values (Source: WHO, 1998).

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<thead>
<tr>
<th>PAH</th>
<th>TEF</th>
<th>PAH</th>
<th>TEF</th>
</tr>
</thead>
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<td>Naphthalene</td>
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<tr>
<td>2-Methylnaphthalene</td>
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<td>Chrysene</td>
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<td>Acenaphthylene</td>
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<td>Benzo(b)fluoranthene</td>
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<td>Acenaphthene</td>
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4.2.14 PCDD, PCDF, and PCB

Sampling for PCDD, PCDF and PCB was conducted in accordance with USEPA Method 23 - *Determination of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzo-p-furans from Stationary Sources* (USEPA, 1995b), using a USEPA Modified Method 5 multicomponent sampling train. This method has been proven to be effective for the sampling of a wide range of other semi-volatile organic compounds from combustion systems, including PCBs and PAHs. The method 23 sampling train for PCDD/F, PCB and SVOCs can be seen in Figure 4.5, with photographs of the general arrangement during site sampling runs seen in Figure 4.6 and Figure 4.7.

Like the PAH modified USEPA Method 5 sample methodology, a pre-spiked XAD-2 resin was spiked (prior to sampling) with isotopically-prepared PCDD/F and PCB surrogate standards on a 10 gram amberlite-polyurethane foam packed column. The surrogate recovery standards used for PCDD/F and PCB individual isomers were in accordance with Table 1 of USEPA Method 23 (USEPA, 1995b) as summarized in Table 4.3.
Figure 4.6: Cement flue gas sampling with a USEPA method 23 sampling train.

Figure 4.7: Cement flue gas sampling with a USEPA method 23 sampling train.
Table 4.3: PCDD/F and PCB isomers spiked within XAD-2 resin and I-TEQ values

<table>
<thead>
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<th>NATO ‘95 I-TEF</th>
<th>WHO ‘05 I-TEF</th>
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<tr>
<td>^13C-PCB-118</td>
<td>2,3′,4,4′,5-Pentachloro biphenyl</td>
</tr>
<tr>
<td>^13C-PCB-123</td>
<td>2′,3,3′,4,4′,5-Pentachloro biphenyl</td>
</tr>
<tr>
<td>^13C-PCB-156</td>
<td>2,3,3′,4,4′,5-Hexabiphenyl</td>
</tr>
<tr>
<td>^13C-PCB-157</td>
<td>2,3,3′,4,4′,5′-Hexabiphenyl</td>
</tr>
<tr>
<td>^13C-PCB-167</td>
<td>2,3′,4,4′,5,5′-Hexabiphenyl</td>
</tr>
</tbody>
</table>
Source gas was isokinetically withdrawn through a heated quartz-glass nozzle and probe liner, and PM is collected on a heated, high-efficiency GFF (encased in the hot box at 120 °C). Organic materials in the gas phase that pass through the GFF are condensed (by recirculating ice-water) and collected within the XAD-2 sorbent cartridge. A condensate knockout trap and series of Greenburg Smith impingers were also located immediately after the sorbent cartridge. Like the PAH sampling methodology, the sampling train was disassembled at the end of each run, washed with toluene and acetone, and sample media (GFF, resin cartridge) preserved during transportation to the NMI laboratory.

In the laboratory, recovery standards were added to the sample components, and are spiked with a range of isotopically labelled surrogate standards. The filter, resin column, impinger solution and washings were extracted with organic solvents, and separated by Hewlett-Packard 5890 high resolution gas chromatography (HRGC) with a DB-5 column (30m x 0.25mm). The bulk measurement of PCDD/Fs, PCBs and dl-PCBs was performed using HRGC coupled with a VG70-S high-resolution electron impact mass spectrometry (HRMS) in accordance with USEPA SW-846 Method 8290a (USEPA, 2007b).

Sample cleaning was effective by partitioning with sulfuric acid then distilled water. Further purification is performed using column chromatography on acid and base modified silica gels, basic alumina and carbon dispersed on celite. This method analyses the molecular ions of each homologue pattern (tetra- to octa-) PCDD (seven) and PCDF (ten) individual isomers, and PCB isomers analysed for non-ortho (four) and mono-ortho (eight) dl-PCBs, shown in Table 4.3. The percentage recovery for $^{13}$C$_{12}$ labelled surrogate standard was assessed against each sample’s corresponding tetra-to-octachlorinated homologues, to quantify the native PCDD/F present in the sample, and to determine R* and Rs efficiencies. Similarly, to SVOC methods, field samples were not used if the surrogate recoveries did not meet the USEPA (1995b) permissible ranges. The normal acceptable criteria for R* efficiencies for tetra-penta-hexa PCDD/F congeners is 40-130%, for hepta-octa PCDD/F congeners is 25-130%, and for PCB congeners is 40-120%. Acceptable criteria for Rs efficiencies are 70-130% for PCDD/Fs and 60-140% for PCBs.
For each sample, the dioxin toxic equivalent (I-TEQ) of each PCDD and PCDF congener was calculated, standardised (at 10% O₂), and referenced to NATO (1995) and WHO (2005) TEF values of 2,3,7,8-TCDD, seen in Table 4.2. The toxic equivalent of each PCB congener was calculated, standardised and referenced to WHO (2005) 2,3,7,8-TCDD TEF. From the sampling results, the UMEF of PCDD/F congeners was calculated (excluding LOD values) for the total of pollutants, total of NATO (1995) I-TEQs, and total of WHO (2005) I-TEQs. The latter two standardisations are referenced within this thesis as PCDD-Natoex and PCDD-WHOex.

The UMEF of PCB congeners was also calculated for the total of dl-PCBs (excluding LOD values) and total of WHO (2005) TEQs (for including and excluding LOD values). These are referenced within this thesis as PCBex, dl-PCB-WHOin, and dl-PCB-WHOex respectively. The NMI laboratory which performed all PCDD/F and PCB analysis estimated its internal accuracy to be 10 wt%. The overall estimated measurement of uncertainty18 for these methods was within ± 15 wt.%.

4.3 Quality control and facilities

The field equipment used for the sampling and analytical methods described above are utilised daily by emission monitoring consultants. Knowledge on the standardised methods and equipment used for monitoring of the analytes has been accumulated by constant reference materials, external testing accreditation audits, and discussions with proficient and experienced industry members.

The standard of quality control of field glassware components used in the multicomponent sampling trains, sampling bottles, Teflon lids, and probe brushes shall be cleaned thoroughly prior to each test with nitric acid, purified organic solvents, de-ionized water, and air-dried as per accordance with USEPA methods. After completion of each isokinetic tests, sample recovery is stored into glass and Teflon washed bottles, and identified. To avoid background contamination, a multicomponent sampling train is only to be used for a single test, and all glassware received a thorough clean and rinse prior to the next test.

In addition to the regular sampling train, an assembled blank train was used to sample an equal amount of ambient air away from the stationary source (and to ensure that no stack
gas was sampled). The recovery of the blank train components (i.e. filter, absorbent, XAD-2 resin, washings) were laboratory analysed so to support the quality assurance for handling, recovery and transportation and provide background levels of contaminated equipment and chemicals.

To provide quality assurance to a test and its results, equipment calibrations on the nozzle, s-type pitot, thermocouple, manometer, thermal indicator, heated probed and filter box, temperature control box, sampling hoses, diaphragm pump, gas meter, balance scales, Testo 350XL gas analyser, and non-isokinetic sampling pumps were regularly conducted and recorded.

4.4 Modelling of the process

The research of optimised ADF co-incineration is designed to examine ADF fuel capabilities and combustion factors that influence the formation and conveying pollutants, signifying the possible development of control technologies and techniques for their emission reduction. The examination on multi-variance data specifically to parameters which influence pollutant formation, kinetics, and suppression can be derived from mathematical equations. The utility of model generation provides a method for small-scale tracking and predicting of combustion emissions, in which may be more appealing to industries (at decision-making) regarding the simple changes to the system rather than later, expensive additional equipment. However, the execution of partial differential equations for large amounts of data and influencing parameters can produce complex and less accurate models.

Examining air pollutant correlations with independent and intervening parameters by mathematical and statistical packages have recently had numerous successful experiments. These studies base computational and functional software to encompass the operating mechanisms and mass balances of a facility, whilst incorporating the multivariate analysis of physical, mechanical and chemical reactions which it undergoes. As this large amount data is complex and not easily interpreted, principal component analysis (PCA) is a data analysis feature which can find out how one data set is different to another, which variables contribute mostly to this difference, and if those variables are correlated (by variable linearity and interaction) or independent.
The extraction of data with PCA allocates variables loading and score vectors, highlighting the interrelationships amongst them all. The weighting of the variables permitted the variables with very little variance to be considered evenly when compared with larger ones, and contribute its influence on the PCA. By detecting a structure in the relationship between variables, the defined principle components are visually quantified by a score plot representation showing samples with similar emissions to be near each other.

The use of multivariate partial least square (PLS) was also used to find critical variables of the combustion process and used to formulate a model for predictive pollutant formation. The mixing of two PCA computations permits PLS to regressional coefficient residual distributions to a model with predetermined levels of significance and associated standardised errors. A fitness for each of the model produced was examined for its goodness of fit by coefficient of multiple determination ($R^2$) and standard error of prediction (SEC). The examination of $R^2$ above a value of 0.75 or greater suggests the model is acceptable for use. The examination of SEC provides the model a standardised deviation of error from the data sets mean. Although PLS is useful for theory confirmation, it can also be used to suggest where relationships might or might not exist and to suggest propositions for later testing.

With PLS somewhat challenged as a soft optimisation technique with serious errors and drawbacks in its methods, the Unscrambler $X^C$ component-based PLS avoids two serious problems when compared to other well-known covariance fitting approaches (generally exemplified by software such as LISREL, EQS, COSAN, and EZPATH), namely inadmissible solutions and factor indeterminacy. A core distinction between these techniques is the use of structural equation models for theory testing and development or for predictive applications. For application and prediction, the Unscrambler $X^C$ PLS approach is more suitable as all measured variance is useful variance and needs to be explained since these are linear combinations of observed measurements. This avoids the indeterminacy of factor score estimations and the subsequent loss of predictive accuracy.

Modelling of NO$_x$ formation by Mullins et al. (2002) and Svinning et al. (1998), of SO$_x$ by Boubel et al. (1994), of PCDD/F, PCBs and polychlorinated benzene (PCBz) by Pandelova et al. (2006), and of PM, CO, CO$_2$, H$_2$O by Sal (2007) have established gas
and particulate formation pathways, which forecast likely rate constants from similar types of reactions.

Mullins *et al.* (2002) utilised a statistical computer package SIRIUS®, (developed by Pattern Recognition Systems) for the generation of empirical models of two complex combustion systems, whereby influencing parameters are identified and allow for the prediction of NOx emissions within an acceptable degree of error. Likewise, Svinning *et al.* (1998) performed PLS analysis of NOx formation during fuel reburning of RDF, TDF and plastics through the statistical program Unscrambler®. Pandelova *et al.* (2006) also utilised a PCA program named Multi-Variate-Statistical Package® (developed by Kovach Computing Service) for the setting of linear combinations between different PCDD/F, PCB and PCBz values, and the correspondence analysis of underlying data structures and influential parameters.

Further to statistical modelling, numerous studies by Cao *et al.* (2010), Zhang *et al.* (2011) and Rahman *et al.* (2014) have incorporated experimental data into Aspen-Plus® simulation software. Cao *et al.* (2010) examined the amount of combustion air needed in the precalciner under 4 different combustion fuel conditions (coal baseline; with 50 wt.% petcoke; with 50 wt.% MBM; and only petcoke, and MBM) with similar process operating parameters. Zhang *et al.* (2011) modelled the precalciner effects of coal-fuel and tertiary air flow rates on the concentration of CO2, CO, NOx, and SO2 emissions. Whereas, Rahman *et al.* (2014) modelled the flow rate effects of three ADF types (TDF, MBM, RDF), energy efficiency and CO2 emissions from the PH tower.

Based on the above, this thesis proposes to utilise a commonly-used steady-state process modelling and simulation software, with a strong focus on thermodynamics and clinker chemistry in the PH/PC-kiln to examine and predict the final impact of co-incineration to material flow, mass balances and emissions. From these small real-world trials, the use of a computerised process model will allow for larger quantities of fuel substitutes be tested. As a lot of information on the design and operations is collected and planned for modelling, the use of Unscrambler X® is most appropriate as an established tool which has been used world-wide in recent decades by data analysts, academic researchers and engineers. The advantage of using this package is that it establishes an accurate steady-
state model from situation analysis and process balancing by using strict and scientific methods based on the material and energy conservation principles of the system.

For this thesis, the modelling of gaseous and particle formation from baseline and ADF co-incineration was performed with the statistical software package Unscrambler X© (developed by Camo, available from http://www.camo.com/). The multivariate data analysis performs the identification and normalisation of key emission-influencing conditions (by PCA), while using underlying data patterns and relationships to generate an empirical model (by PLS). This UMEF was modelled against the 26 plant operating parameters, for each of the 94 baseline and experimental runs. Key influencing parameters are further assessed against each other and contributions to the pollutant UMEF variable, and identified through the statistical modelling components of X-Y loading and of weighted regressional coefficient. Calculated differences to the pollutant profiles is detected through the score and loading plots, noting the subsequent influence of using alternative fuels.

From the normalisation of data relationships and its empirical model generation, this thesis also engages plant operating conditions into a scientific data management program, TableCurve 3D© (proprietary to Systat Software, available from www.sigmaplot.com). The process simulation software is similar to other programs, such as Aspen-Plus, and allows for the plotting of a 3D surface-residual graph to the empirical data points and measured outliers, showing areas its best fit and influence. Plot simulation with this software was done for the fuel-combustion gas pollutants (i.e. CO₂, CO, NOₓ, and SOₓ) and for the key operating conditions that influence pollutant-forming mechanisms.
Chapter 5: Gaseous pollutants during ADF co-incineration

At the time of this research, numerous real-world emission monitoring studies were conducted from 10 differing cement kilns, which operated with various forms of carbonised fuels and ADF substitutions. The monitoring results of gaseous pollutants are attached in Appendix 2, along with key details on the cement plant’s operating conditions, flue gas conditions, fuel types used and the amount of substitution (if any), and the UMEF of the target pollutants.

For a correlation on key operating parameters consistencies across different cement plants, 11 parameters were noticeably constant and included the PH/PC and kiln chamber (gas and material temperatures, and residence times) and the kiln flame (temperature and time). Six other process parameters (seen in Figure 5.1) were shown to have comparative differences, largely due to the plants’ design and physical capabilities. These variables do however have noticeable interrelationship similarities, namely volume of induced air and exhaust gas flow rate; quantity of raw meal used and clinker produced; and fuel firing rate at the kiln and precalciner. The mean and nominal variance shown in Figure 5.1 does also signify that regardless of plant size or production rate, each plant design and functionality remains relative to other operating plants. Figure 5.2 identifies the distribution and variance of the collective plants’ process parameter, through its interquartile range (rectangular box) and suspected outliers. Of significance to emissions monitoring is the variance with kiln fuel rate and standard mass flow (predominately sourced from cement plants B and C).

While all emissions testing was conducted over several hours on different days, the plants’ operating conditions were held close to normal as reasonably possible. Variations in maintaining certain parameters (e.g. temperature, residence time) were observed due to the natural fluctuations of the process and its magnitude. As the rate of induced air has a significant influence, a regressional analysis of its relationship with each sample’s meal-feed and clinker-load rate is plotted in Figure 5.3, showing a consistent correlation during the use of conventional and alternative fuels. The calculated empirical model for the dataset CO₂ UMEF is:

\[ \text{Load} = 1.5485 \times \text{Feed} + 61.944 \]  \hspace{1cm} (5.1)
Figure 5.1: Calibration of cement plant key operating conditions.

Figure 5.2: Operational range of key cement plant process parameters.
Figure 5.3: Correlation of air rate per meal feed and clinker load rates.

From the collection of data from the emissions monitoring, a brief discussion is presented on each gaseous pollutant UMEF results along with the reglossional analysis of key operating conditions and fuel types. Within the graphs presented (including those in Chapters 6 and 7), baseline samples are represented by black square markers and ADF samples by red diamond markers.

5.1 Carbon Dioxide

Monitoring of CO₂ gas within the exhaust stream will vary based on the level of calcination and the complete devolatilisation of the carbonised fuel and any waste material. For the 94 samples, most CO₂ UMEF results are observed to be relatively constant within plants (Figure 5.4), with few having up to 50 vol.% variation. With the substitution trials of waste oil, pasminco sand, wood chips with plastics, and carbon dust, (in cement plants A to E), the CO₂ UMEF was predominately consistent (or slightly below) the respective average baseline results. For these materials, it is shown that the CO₂ UMEF can be different when the fuel type is the same (within a plant, or between plants). For the samples F4, G4 and H4 which each substituted 10 ADF% with wood chips, monitoring results showed a 20 vol.% emission reduction to respective plant baseline samples. This analysis shows a comparative substitute of carbonaceous while still achieving a reduced CO₂ UMEF. Furthermore, this technique is shown to not be further
dependent on downstream control measures as suggested by Zeman and Lackner (2008) such as the injection of sulfur-containing gypsum along with a final carbon capture and storage unit.

Figure 5.4: Measured and calculated CO$_2$ emission factors during baseline and ADF co-incineration.

Given most substitute fuels having a high carbon-hydrogen composition, the increased generation and release of CO$_2$ from co-incineration would be evident if stoichiometric conditions were not achieved. The suppression of CO$_2$ (of up to 30 vol.%) is further supported as the CV of these alternative secondary fuels is similar to that of the coal used (CV=26-30 MJ/kg). For experimental tests with solvents and TDFs (within cement plants F, G, I and J), the CO$_2$ UMEF were either consistent or slightly above average baseline results. Of all the ADF types trialled, TDFs have the largest CV and carbon-content which would be expected to have the most improved CO$_2$ emissions, however this achievement is subsequently influenced by the preference of O$_2$ combining with hydrogen atoms (rather than with the lesser carbon atoms) and cement plants’ lean stoichiometric ratio, extending these emissions to 108-113 vol.%. In comparison (Figure 5.4) to the estimated 534 kg CO$_2$ UMEF published in the National Inventory Report 2011 (DIICCSRTE, 2013) or the European estimated 672 kg CO$_2$ UMEF (EIPPCB, 2013), the
mean value of all tests for each cement plant were either considerably above (for cement plants E, I, J) or below these referenced figures. Apart from TDFs, all ADF runs were either aligned or below this referenced estimate. Quantitively, this reduced UMEF is similar to Stefanović et al. (2010) whereby CO₂ annual emissions from a single facility can be reduced by 76,000 tonnes. Measurements from the PH/PC-kiln systems were however noticeably lower than the Marceau and VanGeem (2011) reported average of 863kg CO₂ UMEF, signifying that some calculated assumptions are possibly unachievable or that target objectives are largely overestimated.

Further to the physical examination, a calculated CO₂ theoretical EF was performed with the facilities operating data as identified in subchapter 2.5.1 and Appendix 1. The extrapolated theoretical CO₂ specific emission (CO₂ SE) for each baseline and ADF sample and plotted in Figure 5.4, showing a comparative increased to the sampled CO₂ UMEF. The gap to this theoretical calculation is observed to be greatest (in cement plants A to E, and H) whereby process moisture content and Oₐ are relatively higher, and are sequentially not included to the calculation steps.

The multivariate analysis of CO₂ UMEF and its relationship with operating parameters identified key contributing conditions whilst generating its empirical model. The regressional analysis (Figure 5.5) plots the predicted UMEF values against field-measured UMEF values, and shows the linearity between operating parameters, baseline or ADF runs, and modelling of predicted values. The calculated regressional line signifies the validity of the model through a level of confidence, and displays the spread of values on either side.
Figure 5.5: Regressional model of CO₂ UMEF.

The modelling of CO₂ UMEF showed a strong regressional relationship with the PCₙ, PH/PC gas and material temperatures, meal feed rate, and clinker produced. As the feed rate of meal and fuel into the system is an important component for clinker production, the effects of CO₂ UMEF can be heavily influence by the balance of ADF use and the achievement of calcination temperatures within the PH/PC tower. The preparation of this supports the further transfer of heat transfer in the kiln, where its completeness is a function of energy input, preheated meal temperature and the shortness of residence time needed to be within the burn zone. Given that the values represent cement plants of differing natures, design, APCD, purpose, age, and maintenance, this plot can still provide an indication on the correlation of co-incinerating ADFs and the subsequent CO₂ emissions (as supported by Sarofim et al. (1994)). The empirical model for CO₂ UMEF is calculated at:

\[
\text{CO}_2 = -276 - 0.04*K_f + 0.004*PC_f - 0.05*ADF_{fl} - 0.02*K_{fr} + 0.06*PC_{fr} - 0.01*ADF_{fr} + 1.48*Feed + 0.89*Load + 0.98*K_{gt} + 0.01*K_{fr,gt} + 0.06*Load_{mt} + 0.81*PH_{gt} - 0.54*PH_{mt} + 0.04*PH_{fr} + 0.78*PC_{gt} + 0.51*PC_{mt} + 0.0005*PC_{fr} - 0.44*K_{gt} + 0.53*K_{mt} - 0.02*K_{fr} - 0.03*Air_r - 0.0002*S_1 + 0.03*O_6 - 0.001*H_2O - 0.03*O_2
\]

From this empirical model, data-specific 3D surface graphs (Figure 5.6) were plotted for CO₂ UMEF against PH/PC gas and material temperatures, and against the meal feed and clinker load rates. Of significance to preheater (Figure 5.6a), achieving a high PH_{mt} through heat transfer of high gas temperatures does produce a greater CO₂ UMEF,
however this does show the optimised reaction for carbonate decomposition, and the further oxidising of any incomplete combustibles (e.g. PM, CO). These attributes are comparable to the precalciner (Figure 5.6b), whereby the high gas and material temperatures are significant to carbonate decomposition and the reduction of pollutants. For the relationship of meal feed and clinker load rates, Figure 5.6c shows CO$_2$ UMEF to be most optimal when clinker load rates are at least 60% of the meal feed rate.

**Figure 5.6:** 3D surface graph for CO$_2$ UMEF against (a) preheater temperatures, (b) precalciner temperatures, (c) meal feed and clinker load rates.

### 5.2 Carbon Monoxide

Monitoring of CO within the gas stream identified the degree of incomplete combustion combined from the various preheater, precalciner and kiln phases. From CO UMEF results (Figure 5.7), baseline levels are shown to be relatively consistent in some cement plants (namely A, B, and H) and inconsistent within others. However, even with varying kilns sizes and operations, the use of all ADFs (excluding waste oil) emitted a similar or reduced CO UMEF to the referenced baseline averages. This is shown more specifically with pasminco sand (64 vol.%), wood chips (40 vol.%), wood chips with plastics (50 vol.%), and carbon dust (65 vol.%). When compared to the European reported emission levels of 0.46 kg CO UMEF (EIPPCB, 2013), most baseline and ADF samples fall below this value, supporting the notion that fuel substitution can support normal cement manufacturing operations.
Figure 5.7: Carbon monoxide UMEF during baseline and ADF co-incineration, and relevance to the sample CO$_2$ UMEF.

Furthermore, Figure 5.7 shows the CO-CO$_2$ UMEF relationship from emissions monitoring, identifying a comparative similarity to the formation and emittance of carbon monoxide and carbon dioxide. Similarities exist within and amongst cement plants, and the relationship identifies the substitution of waste oil, solvents, wood chips and TDF to be most consistent with baseline combustion fuels. This achievement is greatly assisted with the use of in-line flue gas monitoring, determining the ongoing generation and measurement of kiln gas levels (particularly with CO$_2$, O$_2$, CO and NO$_x$). With this, slight adjustments to the kiln and precalciner fuel firing rates and raw meal loading rate can occur so to minimise extreme temperature drops or fluctuations, leading to a slow heterogeneous conversion of char and CO$_2$ formation.

The statistical significance further supports studies published by Prisciandaro et al. (2003) and Axelsen et al. (2003), which showed no statistical effects or modifications to CO emissions with the ADF co-incineration. The results were shown to be an improvement to other studies (Aranda-Usón et al., 2013; Carrasco et al., 2002) which reported significant CO UMEF increases of up to 40 wt.%, but also had a lower PH$_{int}$ and residence
time. As the operating conditions of each PH/PC-kiln is independently dictated by the raw meal composition and clinker specifications, the effectiveness of pollutant formation and DRE is significantly challenging given these pre-requisite constraints. This inherently requires for clinker production to have designated temperature profiles, which subsequently only partially decomposes the fuel or partially oxidize volatilized hydrocarbons (i.e. intended formation of combustion dead spots). Adequate fuel-air mixing and material residence time can alleviate much of this influence.

Specific to TDFs, monitoring results for cement plant J identified the generation of CO to be proportionally increased with the ADF₆% substitution. This is similar to 1.4, 3.0 and 6.0 ADF₆% tyre trials reported by Akkapeddi (2008) and Prisciandaro et al. (2003) with increases of up to 42 vol.% and 30 vol.% (respectively) on baseline CO unit mass emissions. The generation of the additional CO can be due to the less reductive condition of tyres and the required volume of O₂. Like carbon dioxide, the statistical modelling of CO UMEF (Figure 5.8) showed a consistent correlation with factors relevant to incomplete combustion (namely CO₂ and O₂), as well as the PH/PC gas and material temperatures, material residence time, and the mass flow of meal feed and clinker loading. Where an inconsistent meal feed rate or gas-material mixing is shown to occur, dead spots of unburnt fuel are shown to form, leading to increased CO UMEF and other PICs.

![Figure 5.8: Regressional model of CO UMEF.](image)
This correlation is further supported as the fuel-air ratio was stoichiometric to lean (at 1.0 to 1.4) during all plant runs (baseline and ADF) inadvertently increasing the CO UMEF. With the substitution of ADFs which have a lower CV of baseline fuels (and therefore require less O$_2$), complete combustion is more readily able to occur and subsequent CO values were lower than baseline emissions. Results showed the ADF substitution of wood (CV=14-18 MJ/kg) and solvents (CV=18-21 MJ/kg) had a CO UMEF reduction of up to 46 vol.% and 70 vol.% respectively. However, the comparative use of TDF (CV=24-30 MJ/kg) showed only one positive test result (sample J4), even with a stoichiometric fuel-air ratio. The calculated model for CO UMEF is shown to be:

$$
CO = -0.58 - 0.000003*K_f + 0.000002*PC_f - 0.000068*ADF_g - 0.00002*K_f + 0.00004*PC_f - 0.00001*ADF_f + 0.0013*Feed + 0.0007*Load + 0.0004*K_f + 0.00001*K_{f,rt} - 0.00001*Load_{mt} + 0.0003*PH_{gt} - 0.0003*PH_{mt} + 0.000005*PH_{rt} + 0.0005*PC_{gt} + 0.0003*PC_{int} - 0.00001*PC_{rt} - 0.0006*K_{gt} + 0.0003*K_{mt} - 0.00008*K_{rt} - 0.000003*Air_r - 0.000002*S_1 + 0.00002*O_e + 0.00004*H_2O - 0.000006*O_2 + 0.00005*CO_2
$$

Of significance to preheater (Figure 5.9a), achieving a high PH$_{mt}$ through heat transfer of high gas temperatures does produce a greater CO UMEF, however this does show the optimised reaction for carbonate decomposition, and the further oxidising of any other incomplete combustibles (e.g. PM, CO). Furthermore, a high meal temperature under lean fuel-air conditions (Figure 5.9b) is shown to produce higher CO emissions. Under stoichiometric S$_1$ conditions (0.5% - 1.5%, as seen in Figure 2.18), CO UMEF is considerably low in the early cyclone stages where meal temperatures are considerable low (120 - 125 °C), and increases incrementally due to downstream incomplete combustion. As this material progressively moves into the precalciner, Figure 5.9c shows CO UMEF to dually increase where gas and material temperatures are both considerably high, subsequently influenced by the flame temperature, raw feed rate and heat transfer rate. Similar to the results published by Zhang et al. (2011), modelling of precalciner gas residence time against an increasing S$_1$ (between 1.5% - 2.5%) does reduce the generation of CO (Figure 5.9d). However, the balance of these variables does require to incorporate PC$_f$ and O$_e$ parameters, otherwise the offset will generate additional Fuel NO$_x$ pollutants (as shown in Figures 5.12a and 5.12b). In review of complete combustion, Figure 5.9e shows CO generation as additional O$_2$ (through O$_e$) is incorporated into the system.
Figure 5.9: 3D surface graph for CO UMEF against (a) PH material temperature, (b) PH S₁, (c) PC material temperature, (d) PC S₁, (e) O₂ and CO₂ emission volumes.

5.3 Oxides of Nitrogen

The results of NOₓ UMEF (Figure 5.10) showed some natural variations on its formation within and between cement plants, and during normal operations. With reference to European cement plant levels of 0.33-4.67 kg NOₓ UMEF (EIPPCB, 2013); most baseline and ADF samples are concurrently within this range. This is further supported with the reported average of 2.0 kg NOₓ UMEF (Marceau and VanGeem, 2011) from cement plants within the USA. The use of waste oil at 3.5, 5.5 and 7.5 ADF₀ substitutions has shown a similar release of baseline NOₓ UMEF results, and a correlating effect with CO₂ UMEF (Figure 5.4) and CO UMEF (Figure 5.7) values. Karstensen et al. (2016) support this through the online measuring of O₂/CO₂ and CO in the flue gas can help control excess levels of air that would favour NOₓ formation. This is particularly important as the chemical composition and immersed moisture content of an ADF like waste oil could effectively increase the flame temperature, thus allowing fuel NOₓ formation to occur. The use of waste wood has shown a NOₓ reduction of up to 90 vol.% of baseline values, while waste solvents results have an increase (of 20 vol.%) to differing plants’ baseline results.
Figure 5.10: Flue gas NOx UMEF during baseline and ADF co-incineration.

With the substitution of TDF, four NOx UMEF results showed a decrease to baseline sampling of up to 43 vol.%. Under similar operating conditions, sample emissions during co-incineration yielded a better statistical analysis than trials reported by Prisciandaro et al. (2003), whereby NOx concentrations had a significant difference against baseline emissions particularly due to the larger volume of Oe and S1. The results showed similar emissions to other co-incineration trails as reported by Akkapeddi (2008) and Carrasco et al. (2002) which also had a 32 vol.% and 11 vol.%, respectively, improvement to baseline emissions. One result (sample J4) did show an outstanding increase to baseline NOx levels by 80 vol.%, with this sample also correlating to a substantially low CO level of 45 vol.% below the baseline results. The regressional analysis of NOx UMEF (Figure 5.11) modelled a strong correlation with thermal NOx formation (primarily due to precalciner and kiln residence time, Oe and S1) and prompt NOx (from residual water concentration). As the PH/PC-kiln system utilizes a separately-staged combustion philosophy, the calciner’s design is significant in establishing a reducing zone for the decomposing of thermal NOx during waste co-incineration. The program calculated coefficient for NOx UMEF is:
\[ \text{NO}_x = -1.44 + 0.000046*K_f - 0.000053*PC_f + 0.0003*ADF\% - 0.00016*K_{fr} + 0.000068*PC_{fr} + 0.000077*ADF_{fr} + 0.0018*\text{Feed} + 0.00029*\text{Load} + 0.0028*K_f + 0.00001*K_{fr} - 0.00006*\text{Load}_{mt} + 0.0015*PH_{gt} + 0.00018*PH_{mt} - 0.00034*PH_{fr} + 0.0035*PC_{gt} - 0.0019*PC_{mt} - 0.000012*PC_{rt} - 0.0027*K_{gt} - 0.00015*K_{mt} - 0.000048*K_{rt} + 0.000013*\text{Air}_{r} + 0.00001*S_{1} + 0.0002*O_e - 0.001*\text{H}_2\text{O} + 0.00037*O_2 - 0.00057*CO_2 \]

**Figure 5.11:** Regressional model of NO\(_x\) UMEF.

With a high kiln temperature, the formation of thermal NO\(_x\) from the flame is shown to exponentially increase under a lean fuel-air environment (Figure 5.12a) or in-flame oxygen enrichment (Figure 5.12b). As NO\(_x\) formation is greatly dependent on residence time within its optimal temperature range, a reduced atmosphere (i.e. low O\(_2\) content) the is shown to be significantly reduce its UMEF. Relevant to kiln stoichiometric conditions, the increase in NO\(_x\) UMEF is also shown to be dependent of the fuel-air ratio in the precalciner (Figure 5.12c) with additional effects from the amount of O\(_e\) within the vessel (Figure 5.12d). The subsequent influence of this will essentially reduce the availability of fuel-nitrogen and the ratio of nitrogen to oxygen (similar to Axelsen et al. (2003) and Lemieux et al. (2004)). This is further supported by the formation of thermal NO\(_x\) shown to be greatly dependant on the fuel residence time for combustion, subsequent to the amount of excess O\(_2\). Despite a lower flame temperature in the PH/PC when compared to the kiln, Figure 5.12 shows that it can be submissive to conclude that NO\(_x\) UMEF may be maintained while substituting fuel use to the precalciner as suggested by CSI (2006) and Karstensen et al. (2016). Here it is shown that NO\(_x\) emissions can be similar between kiln and precalciner contributions.
Figure 5.12: 3D surface graph for NO\textsubscript{x} UMEF for kiln flame time (with (a) S\textsubscript{1}, (b) excess air), and for precalciner fuel rate (with (c) S\textsubscript{1}, (d) excess air).

5.4 Oxides of Sulfur

The monitoring of SO\textsubscript{x} UMEF under baseline conditions has shown cement plants (A, C, and E to I) operating with emission fluctuations (Figure 5.13). As cement plants primarily utilise a coal-base secondary fuel, the presence of SO\textsubscript{x} formation is evident throughout most baseline emissions. Zevenhoven and Kilpinen (2015) identify SO\textsubscript{x} as the easiest of pollutants to control, with the alkaline pyro-processing environment of a cement plant can be considered as a self-scrubbing mechanism to oxides of sulfur. Baseline samples where many cement plants primarily utilise a coal-base secondary fuel (e.g. plants B, D, E and J) identify the attribute which therefore inductively permits for plants to utilise high-sulphur continuing fuels. However, many experimental samples substituted with a low-sulphur containing ADF (including waste oil, pasminco sand, solvents and tyres) showed SO\textsubscript{x} UMEF to be consistent with (or slightly above) baseline levels, which
largely questions to previous statement. These results are, however, a considerable improvement to the emission results shown by Prisciandaro et al. (2003), whereby SO\textsubscript{x} concentrations during TDF co-incineration were reported at a consistent 42 vol.% higher than baseline levels. If not properly balanced and maintained, an elevated SO\textsubscript{x} UMEF will react amongst themselves and circulate more stable deposits within the preheater which may require shutting down the kiln and clinker production rate.

![Figure 5.13: Flue gas SO\textsubscript{x} UMEF during baseline and ADF co-incineration.](image)

Similar experiments by Carrasco et al. (2002) showed SO\textsubscript{x} UMEF increases by 23 vol.% (1.45 to 1.17 g/kg), which directly influenced by the TDF composition and combustion efficiency (PC\textsubscript{fr} and S\textsubscript{l}) and the generation of CO. Barreto et al. (2008) reviewed emission reduction technologies, showing reduced material temperatures in the PH/PC will permit for sulfur constituents to be released from the raw meal in the later kiln (sintering) stage. This is largely due to the high content of volatiles (54-69 wt.%) within tyres which improves the rate of devolitisation and release of sulphur. With this release being combined with alkali chlorides into clinker, the concentration of sulfur will be less available for flue gas oxidisation and emission.
With 40 wt.% of fuel substituted with general waste (with 5-10 wt.% plastics) and wood chips, there is limited evidence of increased SO\textsubscript{x} UMEF results when referenced against 15 vol.% wood chip substitutes or against baseline emissions. Contrary to Ariyaratne et al. (2013c), the supply of this waste as secondary fuel and its indifference to SO\textsubscript{x} emissions would eliminate the suggested necessity for additional techniques (e.g. oxygen enrichment) to be considered and incorporated. As sulfur is a naturally occurring inhibitor to PCDD/F formation, its absence (or lack of emission) will subsequently show increases to PCDD/F UMEF for these fuel types. CSI (2006) observe that in some instances sulfur or POP inhibitors have been added to the cement kiln so to increase pollutant control.

When reviewed with the TSP, PM\textsubscript{10} and PM\textsubscript{2.5} monitoring, there are some notable correlations with the unit mass emission factor of SO\textsubscript{x}. The regressive analysis on the formation of SO\textsubscript{x} pollutants (Figure 5.14) showed a strong correlation with measured and predicted UMEF values, signifying the key influencing parameters to include PC\textsubscript{fr}, average rate of meal feed and clinker load, O\textsubscript{e} and S\textsubscript{1}.

![Figure 5.14: Regressional model of SO\textsubscript{x} UMEF.](image)

A study by Nielsen et al. (2011) showed similar correlations with SO\textsubscript{x} UMEF and energy inputs whereby the rate of available oxygen is reduced for fuel devolatilization, altering the flue gas composition around the raw meal amount by subtle increases to CO\textsubscript{2} and CO concentrations. In-turn, this will most likely increase the release of sulphur from raw meal
due to reduced conditions, allowing for sulfides and organic sulfur to oxidise into SO$_2$.

The calculated model for SO$_x$ UMEF is shown to be:

\[
\text{SO}_x = -0.078 + 0.0000003*K_f - 0.0000006*PC_f + 0.000006*\text{ADF}_f - 0.00001*K_{fr} + 0.0000003*PC_{fr} + 0.000002*\text{ADF}_{fr} + 0.00008*\text{Feed} + 0.000064*\text{Load} + 0.000064*K_{ft} - 0.0000001*K_{f,rt} + 0.000001*\text{Load}_{int} + 0.00006*\text{PH} - 0.00001*\text{PH}_{int} + 0.000004*\text{PH}_{rt} + 0.0000003*\text{PC}_{gt} + 0.00003*\text{PC}_{mt} + 0.000001*\text{PC}_{fr} + 0.00001*K_{gt} - 0.000024*K_{mt} + 0.000002*K_{ft} - 0.000001*\text{Air}_{rt} - 0.0000003*S_1 - 0.000006*O_e - 0.000009*\text{H}_2\text{O} + 0.000001*O_2 - 0.0000003*S_1 - 0.000006*O_e - 0.000009*\text{H}_2\text{O} + 0.000001*O_2 - 0.0000003*S_1 - 0.000006*O_e - 0.000009*\text{H}_2\text{O} + 0.000001*O_2 - 0.0000003*S_1 - 0.000006*O_e - 0.000009*\text{H}_2\text{O} + 0.000001*O_2
\]

From the empirical model, the setting of a 3D surface graph for SO$_x$ UMEF (Figure 5.15a and 5.15b) shows significant reductions can be achieved through ADF\% co-incineration and its optimal PC fuel firing rate, despite lean or rich S$_1$ conditions. Further to the above analysis, this can be further supported by the fuel proximate and chemical composition having less organic sulfur-containing compounds.

**Figure 5.15**: 3D surface graph for SO$_x$ UMEF and S$_1$ for (a) PC$_{fr}$, (b) total PC$_{fr}$ (including ADF).

### 5.5 Total Volatile Organic Compounds

Monitoring the presence of TVOC UMEF was shown some variation within cement plants and between differing fuel type runs. **Figure 5.16** displays the impartial influence of TVOC generation and release through the co-incineration of low-carbon ADFs (15 vol.% average reduction) when compared to normal operations. The decrease includes the use and increasing ADF\% of waste oil (33 vol.%), pasminco sand (76 vol.%), wood chips with plastics (21 vol.%), waste solvents (31 vol.) and TDF (18 vol.%). The noticeable reduction in TVOC emissions during the co-incineration of pasminco sand was particularly unexpected as its composition was shown to contain organics (initially used
bonding materials) and not subsequently catalyse additional CO emissions. In comparison to other reports of 0.002-0.13 kg TVOC UMEF in Europe (EIPPCB, 2013) or 0.0507 kg TVOC UMEF in USA (Marceau and VanGeem, 2011), the baseline and ADF samples are either sustain or considerably lower than these reported estimates. The TVOC results are further supported and similar to tests reported by Akkapeddi (2008), whereby the substitution of TDF and plastics yielded a UMEF reduction of 32 and 22 vol.% respectively.

**Figure 5.16:** Flue gas organic compounds UMEF during baseline and ADF co-incineration.

The regressional modelling of TVOC UMEF (**Figure 5.17**) identified a key correlation with the kiln flame temperature, kiln fuel calorific value, and the stoichiometric balance of air input, excess O₂, and discharged O₂. The calculated model for TVOC UMEF is:

\[
\text{TVOC} = -0.052 - 0.0000006*K_f + 0.0000001*PC_f - 0.0000007*ADF_{fr} - 0.0000005*K_{fr}
\]
\[
+ 0.0000007*PC_{fr} - 0.0000001*ADF_{fr} + 0.000014*Feed + 0.000006*Load + 0.00003*K_{fr}
\]
\[
- 0.0000001*K_{fr,t} + 0.00000001*Load_{int} + 0.000015*PH_{gt} - 0.0000013*PH_{int} - 0.000002*PH_{fr}
\]
\[
+ 0.000017*PC_{gt} - 0.0000059*PC_{mi} - 0.00000002*PC_{fr} - 0.0000037*K_{gt}
\]
\[
+ 0.0000052*K_{mt} - 0.0000002*K_{fr} - 0.0000001*Air_{fr} + 0.0000000*S_1 + 0.0000001*O_e - 0.0000041*H_2O + 0.0000014*O_2 - 0.0000022*CO_2
\]
5.5.1 Benzene, toluene and xylene

Speciation of TVOC for the individual assessment of BTX concentrations within the flue gas has shown some noticeable variations between kiln runs (Figure 5.18). While there were a substantial number of LOD in the analysis of BTX UMEF, benzene results have shown a comparative increase (9-fold) with the mean use of carbon dust and a contrasting decrease (10-fold) with the mean use of wood chips. A critical evaluation of the results also showed some influence on emissions with the co-incineration of waste oil, wood chips and plastic, solvents and TDFs due a limited availability of catalytic surfaces (from PM, chlorine or metals) and thus pollutant formation. The unit emission of xylene was noticeably similar with each of the ADF materials.

When referenced against all process area temperatures (i.e. flame, kiln, PH/PC, stack), increases to individual benzene UMEF sample results were observed to correlate predominately with an increased preheater gas and material temperature, and flue gas exit temperature. This concurs to the experimental effects studied by Sidhu et al. (2001) on raw meal simulants which were passed over 2 organic precursors (benzene and Myristic acid) and 3 different chlorine-containing catalytic surfaces, each at 300 °C, 400 °C, and 500 °C. These tests were shown to particularly absorb chlorinated-xenlenes, benzenes and phenols on particle surfaces at lower gas temperatures (like the preheater), with decreased the rate of formation as gas temperatures were increased.
Figure 5.18: Flue gas BTX UMEF during baseline and ADF co-incineration.

Results for BTX are also critically elevated with chlorine results (expressed as HCl and Cl₂), indicating that no correlation occurred amongst these emissions rates or the chlorinated formation of benzene and xylene species. Whereas for the analysis of toluene, the use of all ADF maintained consistent release values when compared to the emissions of the kilns’ normal operations. For the statistical analysis of BTX UMEF values with the cement kilns operating conditions (Figure 5.19), the following individual correlations are observed:

1. Benzene – influenced by preheater gas temperature, preheater firing rate, and kiln flame temperature;
2. Toluene – influenced by the mass flow of meal feed and clinker produced, load material temperature, and rate of induced air; and
3. Xylene – influenced by kiln firing rate, preheater gas temperature, fuel-air ratio, and level of excess O₂.

The program calculated model for BTX UMEF is:

\[
BTX = 0.0037 + 0.0000002*K_f + 0.0000001*PC_f - 0.000001*ADF_{\%} - 0.0000005*K_{fr} + 0.0000007*PC_{fr} - 0.0000003*ADF_{fr} + 0.000019*Feed + 0.000009*Load + 0.000008*K_{ft} + 0.0000001*K_{f,fr} - 0.0000009*Load_{int} + 0.000008*PH_{gt} + 0.0000007*PH_{int} - 
\]
0.000002*PH_{rl} + 0.000009*PC_{gt} - 0.0000077*PC_{nt} - 0.0000002*PC_{rt} - 0.000012*K_{gt} - 0.0000007*K_{nt} + 0.0000001*K_{rt} - 0.00000008*Air_{r} + 0.00000002*S_{1} + 0.0000005*O_{e} - 0.0000005*H_{2}O + 0.000001*O_{2} - 0.0000018*CO_{2}

**Figure 5.19:** Regressional model of BTX UMEF.
Chapter 6: Particulate and trace pollutants during ADF co-incineration

This chapter reviews the emission of particulates (as TSP, PM$_{10}$ and PM$_{2.5}$), hydrogen halides and halogens, and heavy metals from several full-scale cement batching plants with the replacement of carbonised energy with an alternative waste material. As mentioned in Figure 1.5 in subchapter 1.2, the reason for undertaking this is to optimise information on existing knowledge gaps by determining ADF impacts on:

- the generation (and emission) of target pollutants;
- varying the ADF substitution rate; and
- key operating parameters.

Monitoring results of these target pollutants (under baseline and experimental conditions) are attached in Appendix 2, along with details of plant key operating conditions, flue gas conditions, and fuel types used and the amount of substitution (if any). Similar to Chapter 5, the plants’ operating conditions were held close to normal as reasonably possible with some variations occurring due to natural process operations.

6.1 Particulate Matter

Similar to TSP results presented by Tiwary et al. (2014), mass emissions monitoring during ADF trials were shown to be consistent with baseline operations at differing kilns (Figure 6.1) whilst operating under normal conditions. In summary, it is evident that pollutant increases occurred in kiln D (159 wt.%) and kiln E (172 wt.%) due to fuel type variations, whereas consistent pollutant decreases were recorded in kiln C (53 wt.%), kiln G (49 wt.%) and kiln H (56 wt.%). These values are also statistically comparative to the USA average plant emission of 0.152 kg TSP UMEF (Marceau and VanGeem, 2011). As the TSP UMEF is dependent on raw meal composition, process characteristics and APCD effectiveness, variations amongst these differing facilities is partially anticipated. Furthermore, as variations amongst APCD efficiencies exists due to its design and operations, a key component to TSP UMEF reduction remains to be greatly dependant on gas temperature, particulates’ aerodynamic size and its distribution within the flue gas.
Specific to ADF fuel type, the average TSP UMEF was identified to be greater than baseline emissions through the substitution of pasminco sand (134 wt.%), wood chips (90 wt.%), plastic (123 wt.%), and carbon dust (58 wt.%). Monitoring results also identified reduced TSP emissions values through the co-incineration of waste oil (59 wt.%), waste solvents (79 wt.%), and TDF (19 wt.%). Specific to TDFs, there is a noticeable reduction to TSP UMEF for all samples when referenced against Carrasco et al. (2002) value of 0.2898 kg/t. The increased ADF% substitution has shown little to no residual effect on the TSP UMEF, with trial runs in cement kilns A and B resulting in a decreased UMEF. For the 5 ADF tests with either 10 wt.% wood chips or 7 wt.% waste solvent substitutions, the emissions were shown to be consistent whilst being trialed across differing cement plants.

The regressional analysis of TSP UMEF (Figure 6.2) for all kilns showed a strong correlation with complete carbon combustion (CO₂ and O₂), and with other influences from the precalciner fuel caloric value, ADF% substituted, the precalciner firing rate (both baseline and ADF), and fuel-air ratio. Surprisingly, the output also displayed that predominate parameter which influences the lower generation of PICs is the effects of
residence time (gas, material and flame), and the preheater as the influencing area. The program calculated model for TSP UMEF is shown to be:

\[
TSP = 0.4 + 0.000078*K_f - 0.00003*PC_f + 0.0003*ADF_{fr} - 0.00004*K_{fr} + 0.000006*PC_{fr} + 0.00006*ADF_{fr} + 0.00062*Feed + 0.00025*Load - 0.00031*K_{fr} + 0.0000038*K_{fr} + 0.00007*Load_{int} + 0.00035*PH_{gt} - 0.00062*PH_{int} - 0.00009*PH_{fr} + 0.0004*PC_{gt} - 0.0004*PC_{int} - 0.00001*PC_{rt} - 0.00039*K_{gt} + 0.00015*K_{int} - 0.00001*K_{rt} - 0.0000034*Air_{fr} - 0.0000005*S_{fr} + 0.000032*O_{e} - 0.000001*H_{2}O + 0.0001*O_{2} - 0.00018*CO_{2}
\]

Figure 6.2: Regressional model of total particulate UMEF.

6.2 PM\textsubscript{10} and PM\textsubscript{2.5}

For the monitoring of PM\textsubscript{10} and PM\textsubscript{2.5} during baseline operations and ADF trials, Figure 6.3 displays the respective concentration levels as generated by the differing cement kilns. Similar to the TSP measurements plotted above in Figure 6.1, the formation and release of PM\textsubscript{10} and PM\textsubscript{2.5} are noticeably constant (or reduced) in most kilns with the supplement of an ADF, and with the increased ADF\% for example, 2 trials with TDF at 7.6 wt.% and 19 wt.% had no change in the effects to baseline emissions, while 1 trial with TDF at 14 wt.% had a reduction to baseline emissions (despite no changes to its APCD). Like TSP, the monitoring of PM\textsubscript{10} and PM\textsubscript{2.5} has also shown an increase of emissions from kiln D (151 wt.%, 182 wt.%) and kiln E (154 wt.%, 182 wt.%), and a decrease of average concentration levels from the co-incineration of pasminco sand, wood chips, plastics, and carbon dust.
Bapat (2001) studied the effectiveness of ESP-baghouse combination, showing the collection effectiveness to reach up to 100% for particle sizes >1 µm. Given the APCDs used were ESPs only (for plant D) and ESP-baghouse combination (for plant E), significant differences for PM$_{10}$ and PM$_{2.5}$ UMEFs would therefore be expected. From the monitoring of TSP and PM$_{10}$/PM$_{2.5}$, a plot of its ratio during the use of fuel types (Figure 6.3) shows the dust size fraction to be significant less than that suggested by EIPPCB (2013). Relative to TSP:PM$_{2.5}$, it is shown to have a relative proportion of 10-30 wt.% (regardless of APCD type) with minor variations between samples. Whereas the ratio of TSP: PM$_{10}$ is shown to have a larger dust fraction of 30-60 wt.%.

Similarities between samples are shown to be more so with plants D and J (using ESPs), and sample irregularities are evident within plants E, F, G, H and I despite the fuel type used (conventional or ADF) or the APCD (singular or combined).

**Figure 6.3**: Flue gas PM$_{10}$ and PM$_{2.5}$ UMEF (and ratio to TSP UMEF) during baseline and ADF co-incineration.
For the regression analysis of PM$_{10}$ and PM$_{2.5}$ emissions, both outputs also provided similar correlations with CO$_2$ and O$_2$, and other influences also from precalciner fuel caloric value, ADF$\%$, precalciner firing rate (both baseline and ADF), average meal feed and clinker load rates, and excess oxygen. The program calculated model for PM$_{10}$ UMEF is:

$$PM_{10} = 0.096 + 0.00003*K_f - 0.000012*PC_f + 0.000016*K_{fr} + 0.000037*PC_{fr} + 0.000025*ADF_{fr} + 0.000027*Feed + 0.00012*Load - 0.0001*K_f + 0.0000014*K_{fr} + 0.000025*Load_{mt} + 0.00016*PH_{gt} + 0.000025*PH_{ml} - 0.000035*PH_{rt} + 0.00017*PC_{gt} - 0.00016*PC_{mt} - 0.0000045*PC_{rt} - 0.000016*K_{gt} + 0.000007*K_{mt} - 0.0000068*K_{rt} - 0.000015*Air_f - 0.0000004*S_1 + 0.000013*O_e - 0.000004*H_2O + 0.000044*O_2 - 0.000067*CO_2$$

Whereas the calculated model for PM$_{2.5}$ UMEF is shown to be:

$$PM_{2.5} = -0.0012 + 0.0000088*K_f - 0.0000037*PC_f + 0.000036*ADF_{fr} - 0.000005*K_{fr} + 0.0000015*PC_{fr} + 0.0000084*ADF_{fr} + 0.00009*Feed + 0.00004*Load - 0.00002*K_{gt} + 0.0000004*K_{rt} + 0.0000008*Load_{mt} + 0.000053*PH_{gt} + 0.000075*PH_{ml} - 0.00001*PH_{rt} + 0.000066*PC_{gt} - 0.000004*PC_{mt} - 0.0000013*PC_{rt} - 0.000048*K_{gt} + 0.000026*K_{mt} - 0.000028*K_{rt} - 0.0000005*Air_f - 0.0000002*S_1 + 0.0000028*O_e + 0.000018*H_2O + 0.000013*O_2 - 0.000021*CO_2$$

From these models, the plotting of predicted versus measured values for PM$_{10}$ and PM$_{2.5}$ displayed similar results to the above TSP results (subchapter 5.2.1). The values of these two parameters present similar ADF tests results (e.g. A4, B3, B6, D9, D10, E9, E10, E11, G4, H4, I6, J8, J12) which have a substantial correlation between the prediction model and real world emissions. Between the imperial models for TSP, PM$_{10}$ and PM$_{2.5}$ a great similarity to each operating parameter is shown to exist, and that its influential relationship towards each pollutant emission is also somewhat similar. This is of importance as all particulate matter (despite its aerodynamic diameter) has the potential detrimentally impact on the adoption and transport of other pollutants (such as metals, dioxins, or PCBs).

6.3 Hydrogen Halides and Halogens

The monitoring of fluorides identified a minor presence of compounds within the flue gas, with this being predominately undetected in most cement plants and amongst all fuel types (Figure 6.4). These results also align with average cement emission reports of 2.3 g HF UMEF in Europe (EIPPCB, 2013) and 0.065 kg HCl UMEF in USA (Marceau and VanGeem, 2011). For plant J, the samples did display some presence of fluorides; however, the use of TDF was shown to have a decreased emission level by 15 vol.%. For
sample E11 (carbon dust), the noticeable increase in HF UMEF is shown to be primarily due to the inert composition of the raw meal and ADF however this is not necessarily the same for same D11 which was loaded at the same PCfr and ADF%. Nevertheless, given the generally low UMEF of HF and fluorine, it is shown that much of fluoride is either captured in the clinker material or has reacted in the kiln to form calcium fluoride.

As chlorine also naturally exists in raw meal in small amounts, the co-incineration of chlorine-containing fuels during cement production needs to be carefully monitored and managed so that implications to clinker quality do not occur. Emissions monitoring of co-incinerating chloride-containing fuels (e.g. waste oil, plastic, TDF) has shown some variations within each kiln run, similar ADF trials in different kilns, and amongst varying fuel types (Figure 6.5). The monitoring did however show that the combustion of wood with plastics and TDF, chlorine UMEF increased (by 26 vol.% and 89 vol.% respectively) as reported by CSI (2006). Furthermore, the increased substitution in ADF% also showed an increased UMEF of chlorine (e.g. plant H and plant J) primarily due to higher gas temperatures in the kiln and PH/PC, inhibit the later ability for its condensation to other particles (including the smaller PM10 and PM2.5).

As the effects of chlorine-contained alternative fuels have contradicting publications, its cause and effects to clinker material and the formation of other hazardous pollutants requires greater discussion. Karstensen (2008a) suggests the chlorine content in raw meal or combustible fuels is not enough to form POPs under unfavorable conditions. Furthermore, the use of cement manufacturing proposes to scavenge and encompass any free chlorine through the highly alkaline environment, thus making it absent for further chlorination of organic materials (Sidhu et al., 2001).

Process monitoring of PHgt and PCgt (Attachment 2) shows incremental peaks of HCl emissions (which includes Cl2) when gas temperatures are higher in the preheater and precalciner. With chlorine capture being less effective at these high temperatures, this allows for its later catalysts in forming PCDD/Fs at the lower temperatures of the APCD. Sidhu et al. (2001) identify the predominate chlorine present in the preheater cyclones will be organic chlorides, HCl, Cl2, alkali chlorides, and transition metal chlorides. This is supported by Dellinger et al. (1993), adding that the capture of chlorine is less achievable under high alkaline temperatures, allowing for the conversion of HCl to Cl2.
Given this, the initial input and thoroughfare of chlorine (and its ratio to sulfates) during cement manufacturing should still be monitored and controlled so to minimize any process upsets and its affiliation with PM.

**Figure 6.4:** Flue gas hydrogen fluoride UMEF during baseline and ADF co-incineration.
The statistical analysis of hydrogen halides and halogens (Figure 6.6) showed similar regresional correlations primarily with the average meal feed and clinker load rates, kiln flame and gas temperature, PH/PC gas temperatures, and S1. The program calculated regression coefficient for fluoride emissions is shown to be:

\[
HF = -0.019 - 0.0000003*K_f + 0.00000001*PC_f - 0.0000004*ADF_{fr} + 0.00000002*K_{fr} + 0.0000001*PC_{fr} - 0.0000001*ADF_{fr} + 0.000001*Feed + 0.000001*Load + 0.0000001*K_{fr} + 0.0000003*K_{fr} + 0.0000004*Load + 0.0000003*PH_{gt} - 0.0000008*PH_{mt} + 0.0000003*PH_{rt} + 0.0000034*PC_{gt} + 0.0000017*PC_{mt} + 0.0000007*PC_{rt} - 0.0000002*K_{gt} + 0.000001*K_{mt} + 0.0000002*K_{rt} + 0.0000001*Air_{fr} - 0.0000001*PC_{gt} + 0.0000001*PC_{mt} + 0.0000001*PC_{rt} - 0.000016*K_{gt} + 0.0000074*K_{mt} - 0.000009*K_{rt} + 0.0000002*Air_{fr} - 0.0000001*S_{1} + 0.0000001*O_{e} + 0.0000001*H_{2}O - 0.0000001*O_{2} + 0.0000003*CO_{2}
\]

Also, the program calculated regression coefficient for chloride emissions is shown as:

\[
HCl = -0.13 - 0.000002*K_f - 0.0000003*PC_f + 0.0000005*ADF_{fr} - 0.0000006*K_{fr} + 0.0000011*PC_{fr} + 0.0000002*ADF_{fr} + 0.000018*Feed + 0.0000084*Load + 0.000005*K_{fr} + 0.0000002*K_{fr} + 0.0000024*Load + 0.000031*PH_{gt} - 0.0000059*PH_{mt} - 0.0000003*PH_{rt} + 0.000042*PC_{gt} + 0.0000086*PC_{mt} + 0.0000003*PC_{rt} - 0.000016*K_{gt} + 0.0000074*K_{mt} - 0.0000009*K_{rt} + 0.0000002*Air_{fr} - 0.0000001*S_{1} + 0.0000008*O_{e} - 0.0000021*H_{2}O + 0.0000006*O_{2} - 0.0000003*CO_{2}
\]
Figure 6.6: Regressional model of hydrogen halide and halogen UMEF.

6.4 Heavy Metals

For the monitoring and analysis of the 14 heavy metals (and their compounds) described in subchapter 2.1.2, the results (Appendix 2) show the co-incineration of ADF has limited partial influence on the particulate and gaseous release of antinomy, As, Ba, Be, Cd, \( \text{Cr}^{3+} \), \( \text{Cr}^{6+} \), Cu, and Mn. For these substances, the limiting effect of emissions is dually to their volatility and the alkaline PH/PC-kiln environment which has a strong chemical affinity in bonding them into the clinker material. The compositional analysis of certain alternative fuels details a limiting contribution of metals (e.g. Sb, As, Cd, \( \text{Cr}^{3+} \), \( \text{Cr}^{6+} \)) already entering the kiln via the raw meal and conventional fuel use. With its introduction being by fuel or meal, the state of the metal compounds is therefore only shown to be changed into CKD, clinker material or within flue gas emissions (Ishikawa and Herat, 2012; Lee et al., 2015; Oerter and Schneider, 2010).

Concurrent to Pipilikaki et al. (2005), the calculated UMEF for total heavy metals (Figure 6.7) from co-incinerating waste oil, waste solvents and TDF showed a similar bassline emission consistent with the use of coal and that no undesirable compounds (e.g. volatiles, \( \text{Cr}^{6+} \), zinc) were formed and released. There was, however, some ADF trials which resulted in the emanation of Fe (86 wt.%), Pb (20 wt.%), Hg (62 wt.%), Ni (12 wt.%), and Zn (93 wt.%). Sarofim et al. (1994) reported similar results whereby these
vaporised metal compounds were shown not to have condensed or been entrapped into clinker material, and subsequently released with the flue gas. With coal being a natural source of certain metal compounds (e.g. Be, Hg), the co-incineration of certain waste materials will decrease the initial input of these compounds, subsequently resulting in a reduced UMEF.

Measurements on As, Be and Cd were noticeable similar for all experimental samples, with the UMEF statistical mean and variance being considerably less than baseline UMEF. As antimony and beryllium is not a common inert residual in fuel composition, an elevated detection would be highly unexpected if the PH/PC-kiln was operating in a truly steady-state condition. Whereas cadmium is a semi-volatile substance and its movement within the PH/PC-kiln and exposure to high temperatures in the sintering zone would expect a promoted volitisation and a possible elevated UMEF. For these compounds, co-incineration of the selected ADF types showed no evidence of increased emissions. Furthermore, at two independent cement plants it is shown that the use of waste solvent (samples F9 and G9) which contains trace elements of Be and Cd, had no detection of its release in flue gas. With cadmium being a semi-volatile substance, its movement within the PH/PC-kiln and exposure to high sintering temperatures would promote its volitisation and subsequent release. However, with no detected emissions the introduced compound is shown to be absorbed into the clinker material (as suggested by Rocha et al., 2011).
For iron oxide, the monitoring results of waste oil (38 wt.%) solvents (15 wt.%) and TDF (32 wt.%) were similar to that of TSP UMEF where comparable values had decreased. However, co-incinerating wood chips, wood chips and plastics, and carbon dust had a noticeable increase to baseline fuels (like TSP results). This finding is concurrent with other experiments (Guo and Eckert, 1996; Eckert et al., 1999) who used a similar or more contaminated ADFs, identifying key contributions of metals were subsequently introduced from the raw meal. From the statistical modelling program, the parameters which had the strongest correlation were the preheater and precalciner residence time, precalciner gas and material temperatures, kiln calorific value, kiln flame temperature, and average clinker produced.

With its composition in most ADF types, Pb compounds are predominately incorporated into clinker, with the remaining part volatizing in the sintering zone and precipitating downstream with CKD and absorbed within the APCD. A key issue with the absorption of semi-volatile compounds (like Pb) is the formation of other low-temperature facilitating compounds such as alkali chlorides and sulfates, leading to possible production disruptions from build-ups of coatings or PH/PC blockages. Therefore, maintaining a consistent flow rate and gas-material temperature is essential to reduce
pollutant formation and possible circulating impacts to the clinker production rate (Karstensen et al., 2016; Rocha et al., 2011).

For the monitoring mercury and its compounds, the air emission results showed a respective average of 9.98x10^{-06} and 2.24x10^{-05} kg Hg UMEF for baseline and ADF tests, all of which are significantly below the Marceau and VanGeem (2011) reported average of 6.94x10^{-05} kg Hg UMEF. For the ADF trials, most results were consistently low (close to the limits of detection) except for samples D8, D9, D10, D11 and J4, where the UMEF was slighted elevated than its comparative baseline emission. As Hg is the most volatile compound in the PH/PC-kiln it would be most certainly released as emissions rather than its entrapment to clinker material or CKD, however as it is vaporised at low or fluctuating temperatures, most of this uptake is expected to be onto particulates in the coal raw mill or at the fuel firing location (i.e. kiln’s hotter end or PC).

Furthermore, low Hg values were particularly shown during the co-incineration waste oil (kilns A, B, C), woodchips, solvents, or TDF (excluding outlier sample J4) whereby the PH/PC-kiln atmosphere would aid the oxidising of this compound by homogeneous or heterogeneous reactions, and most likely with hydrogen halogens. Like other studies (Karstensen, 2004a; Mlakar et al., 2010; Schneider et al., 2011) the statistical variance between sample results showed most gaseous Hg to be absorbed on raw meal particles in the PH/PC, and removed from the gas stream through the APCD. This is shown to be greatest where the exiting flue gas was at a lower temperature, allowing for the greatest extent of Hg condensation. Lechtenburgh (2013) correlation of this relationship shows the greatest reduction of Hg is achieved with APCD gas temperatures of <140 °C. Collectively, this will allow for the raw meal and APCD to cause temporal interruptions of Hg flows with its UMEF levels shown to not be substantial, therefore limiting adverse effects to human health.

When standardised to 7% O₂, the sampling data is shown to be consistent with the Air Control Techniques (2002) report whereby the mean Hg concentration was at 7.24 µg/Sm³ (for conventional fuels) and 14.3 µg/Sm³ (for ADF trials). Similarly, as these cement plants also used differing APCD techniques, the mean Hg concentration for kilns using ESP was at 16.8 µg/Sm³ (7% O₂), however kilns using a duel ESP-baghouse combination had a further reduced result of 5.50 µg/Sm³ (7% O₂). The regressional
analysis of the Hg emissions against the kiln operating conditions has shown primary
correlations with the mass flow of meal feed and clinker loadings, precalciner firing rate,
rate of induced air, and the released CO₂ and O₂ measurements. Where an increased
release of Hg is likely, a reduction of its inert composition being used would be required,
otherwise a reduction to the ADF% firing rate at the precalciner.

Monitoring of nickel (and its compounds) with cement kilns burning conventional and
alternative fuels also displayed large variations within and amongst all samples. Although
Ni is generally present in raw material and fuels at low concentrations, its mean mass
emission rate amongst all cement plants was at 0.248 mg/sec (with conventional fuels)
and 0.249 mg/sec (during co-incineration of ADFs). This is however statistically less than
test results published by Mantus et al. (1992) of 17.3 mg/sec and 11.0 mg/sec for
respective fuel types, detailing the substantial improvement in plant design, operations
and pollution control. For five of the cement kilns (plants A to E), emissions of nickel
were shown to be consistently low (towards LOD) for both baseline and ADF co-
incineration. Even though the remaining five cement kilns had large variations of values
form baseline fuels, the emission values for the ADF trials were subjectively within this
range. As a non-volatile compound, the regressional analysis of Ni concentration
identified a strong correlation with the preheater and precalciner gas temperature, kiln
calorific value, and kiln flame temperature.

The results for zinc emissions during the co-incineration of waste tyres were somewhat
inconsistent with some studies and the literature review. Given the generally high
concentration of zinc in waste tyres, the co-incinerating of TDF was expected to yield
high emission levels and increase with the change of ADF% substitution. Instead the
results showed the use of TDF (mean of 2.07x10⁻⁴ kg Zn UMEF) is consistent with
baseline carbonised fuels (mean of 1.52x10⁻⁴ kg Zn UMEF), and that the emission of zinc
compounds can decrease proportionally with an increase of waste tyres. Tests at plant I
decreased from 0.19 to 0.086 g Zn UMEF when con-incineration increased from 5.5 to
8.1 ADF%, and plant J tests decreased from 0.29 to 0.22 g Zn UMEF with an increase of
14 to 19 ADF%. The effects to clinker quality may, however, need further evaluation
doing TDF co-incineration as shown by Puertas and Blanco-Varela (2004) where the
chemical composition had an increase to Zn content across 2 manufacturing plants.
Test results on zinc concentration during the co-incineration of waste oil was, however, consistent with other literature whereby the ADF values (of samples A4, B3, B6, C7) were slightly increased above baseline mean values. Overall, the mean emission rate of zinc compounds was at 0.766 mg/sec (with conventional fuels) and 1.5 mg/sec (during co-incineration of ADFs), which is also statistically less than that reported by Bhatti (2011) of 2.97 mg/sec and 1.53 mg/sec for respective fuel types. This is further support by a kiln which is operating in a truly steady-state condition will maintain a constant total mass of each metal.

For the regresional analysis of total metals (Figure 6.8), the results indicate that no statistically significantly differences exist in the UMEF of total heavy metals during co-incineration or when used under normal operating conditions. The regresional analysis indicated the primary effects were subjective to material residence time (in the PH/PC tower), precalcer gas and material temperatures, precalcer firing rate, kiln calorific value, kiln flame temperature, fuel-air ratio, and the effects of complete combustion (and therefore retained within the clinker material). The program calculated model for total heavy metal UMEF is:

\[
HM = 0.033 + 0.0000014*K_f - 0.0000002*PC_f + 0.0000016*ADF_f - 0.0000006*K_{fr} + 0.0000001*PC_{fr} + 0.0000003*ADF_{fr} + 0.00001*Feed + 0.000004*Load - 0.0000085*K_{gt} - 0.0000001*K_{fr} + 0.0000002*Load + 0.0000007*PH_{fr} + 0.00000042*PH_{gt} - 0.000003*PH_{fr} - 0.000002*PC_{gt} - 0.000001*PC_{fr} - 0.0000003*PC_{fr} - 0.0000074*K_{gt} + 0.0000013*K_{fr} + 0.0000001*K_f - 0.00000001*Air + 0.00000001*S_1 + 0.00000001*O_2 + 0.0000009*H_2O + 0.0000017*O_2 - 0.0000028*CO_2
\]
Figure 6.8: Regressional model of heavy metal UMEF.

The findings above are consistent with several other publications (Bhatt, 2011; Eckert et al., 1999; Guo and Eckert, 1996), which shows most metal compounds occur as a trace element in raw material or conventional fuels (e.g. pet coke, fuel oil), and are encompassed predominately within the clinker product or CKD. Dellinger et al. (1993) and Trezza and Scian (2000) further show similar UMEF findings with the greater concentration of volatile metals (like Sb, Cd, Pb, or Hg) are in the kiln dust while other refractory metals (e.g. As, Ba, Ba, Cr⁶⁺, Ni) is more present in the clinker material.

This study has shown that certain compounds are added to the process through selected fuels, and that semi-volatile metals can conclusively be released as a fine particle, attached to a fine particle or as a volatile gas. Because there is no specific control to the emission of metals other than chemical and physical properties of cement manufacturing or its downstream APCD, it is therefore important to limit its compositional input from selected ADF.
Chapter 7: Inorganic pollutants during ADF co-incineration

Chapter 5 and chapter 6 detailed respectively gaseous pollutants and particulate and trace pollutants emitted from numerous PH/PC-kilns under baseline and experimental fuel conditions. Similarly, this chapter reviews the UMEF of PAH, PCDD/F and PCB congeners from the same cement producing facilities whilst under similar operating and fuel use conditions. Monitoring results of pollutant emissions at the various facilities are attached in Appendix 2, along with details on its operating parameters and conditions.

7.1 PAH

The monitoring of each cement kiln flue gas for total PAHs during baseline (Figure 7.1) has provided mass emission levels consistent to PM results, specifically with the co-incineration of waste oil (no change), pasminco sand (reduced by 27 wt.%), waste solvents and TDF (both reduced by 90 wt.%). As the chemical composition of tyres contain chlorine and potassium amongst other compounds, the UMEF reduction of total PAH is significantly less the 0.0000124 kg/t as reported by Carrasco et al. (2002).

Figure 7.1: Flue gas total PAH UMEF and PAH BaP$_{eq}$ UMEF during baseline and ADF co-incineration.

The burning of wood chips, wood chips with plastics, and carbon dust, were shown to have an elevated UMEF for both total PAHs and individual BaP-TEQ congeners These
results are consistent with the TSP monitoring results, literature review and other studies, as the use of these man-made wastes which introduce catalytic materials to generate undesirable pollutants and possible bottlenecks to clinker production.

Of the individual congeners with a BaP-TEQ value (and the excluding or including LOD WHO ’95 values), there was a consistent increase due to the above mentioned substituted ADFs, however decreases in Benzo(a)anthracene (83 wt.%) and Benzo(b/k)fluoranthene (95 wt.%) were observed through the combustion of waste solvents and TDF. Even with these noticeable influences, there remained an elevated increase to the emission of the BaP congener across the co-incineration of all ADFs. For the regressive analysis of total PAH UMEF (Figure 7.2), the output indicated key correlating parameters similar to those effecting TSP, including the precalciner calorific value and firing rate, ADF% substituted, and fuel-air ratio. The calculated model for total PAH UMEF is:

\[
\begin{align*}
\text{PAH} &= 0.000056 + 0.00000001*K_f - 0.000000007*PC_f + 0.00000007*\text{ADF}_f - 0.000000006*K_{fr} - 0.000000006*PC_{fr} + 0.00000002*\text{ADF}_{fr} - 0.000000007*\text{Feed} - 0.00000002*\text{Load} - 0.000000001*K_{ft} + 0.000000002*\text{ADF}_{ft} - 0.000000007*\text{Load}_{ft} - 0.00000001*\text{PH}_{gr} + 0.00000005*\text{PH}_{ifr} - 0.00000001*\text{PH}_{fr} + 0.00000003*\text{PC}_{gr} - 0.00000001*\text{PC}_{ifr} - 0.000000008*\text{PC}_{fr} - 0.00000002*\text{K}_{gt} - 0.00000002*\text{K}_{ifr} - 0.00000003*\text{K}_{ft} - 0.000000001*\text{Air}, - 0.0000000005*\text{S}_{1} + 0.000000006*\text{O}_{e} - 0.00000001*\text{H}_{2}O + 0.00000001*\text{O}_{2} - 0.00000003*\text{CO}_{2}
\end{align*}
\]

**Figure 7.2**: Regressional model of total PAH UMEF.

With the analysis of the relevant PAH congeners with a toxic equivalency value referenced to benzo(a)pyrene (excluding limits of detection), Figure 7.2 shows a decrease
in PAH generation with most waste oil trials, however a significant influence remains with the combustion of waste wood chip fuels. Like total PAHs, the regression analysis of PAH BaP\textsubscript{ex} emissions for all kilns indicated a correlation with the same operating parameters (less the precalciner firing rate). The calculated model for PAH BaP\textsubscript{ex} UMEF is:

$\text{PAH BaP}_{\text{ex}} = 7.23 + 0.093*K_f - 0.08*PC_f + 0.12*\text{ADF}_{fr} - 0.06*K_{fr} - 0.032*PC_{fr} + 0.12*\text{ADF}_{fr} + 0.00044*\text{Feed} + 0.0052*\text{Load} - 0.085*K_{fr} + 0.0062*K_{fr} - 0.0038*\text{Load}_{int} - 0.048*PH_{gt} + 0.033*PH_{int} + 0.0022*PH_{nt} + 0.00019*PC_{gt} - 0.035*PC_{mt} - 0.057*PC_{rt} + 0.015*K_{gt} - 0.017*K_{nt} - 0.013*K_{nt} - 0.0091*Air_{f} - 0.0022*S_{1} - 0.016*O_{e} - 0.031*H_{2}O + 0.059*O_{2} - 0.07*CO_{2}$

### 7.2 PCDD/F

With cement plants shown to be an effective process with co-incineration, it also remains to be viewed by communities as a major source of PCDD/Fs. The UMEF of PCDD/F congeners (excluding LOD) under normal operating conditions is shown to be consistent amongst kiln runs and between differing kilns (Figure 7.3), as well as complying with the internationally-adopted EC Directive concentration of 0.1 ng I-TEQ/Nm\textsuperscript{3}. The mass emissions of PCDD\textsubscript{ex} during ADF trials also show some consistency with baseline carbonised fuels and during the increase of fuel substitution. Of interest is the consistent increase of PCDD\textsubscript{ex} levels with the combustion of waste oil (26 wt.%), wood chips (95 wt.%), and wood chips with plastics (219 wt.%).

As molecular chlorine plays a significant role in the formation of PCDD/Fs through a series of heterogeneous reactions and chlorinating aromatic precursors, a comparative evaluation to halide and halogen samples (Figure 7.3) indicate noticeable elevated emissions predominately with the use of conventional coal (i.e. samples A3, C2, D1, E2, E3, F3, F5, F6, F8, G5, G6, H1, H3, H5, I1, I2, I8, J5, J6, J7, J9, J10, J11). This is not necessary the same with the co-incineration of chlorine-containing fuels such as waste oil (in Plants A, B and C), wood chips (Plant H only) and with solvents (Plants F and G), whereby the highly alkaline precalciner maintains a chlorine-lean environment and is unavailable for the chlorination of organic material. This supports field experiments by Lanier (1996) which showed approximately 97% of acid gas was suppressed by an alkaline environment regardless of chlorine feed rate, and that PCDD/F emissions had no change. Babushok and Tsang (2003) and Altarawneh et al. (2009) further examined the generation of highly-chlorinated benzenes in the gas phase whereby the initial chlorine
concentrations were low, identifying the synoptics of PCDD/F being primarily due to poor mixing and the presence of other chlorinated phenol precursors being within a fuel-lean environment.

**Figure 7.3:** Flue gas total PCDD$_{ex}$ UMEF (shown against hydrogen chlorides) during baseline and ADF co-incineration.

Of interest is the distinguished reduction (similarly to PAHs) of PCDD/F congeners to baseline values through the co-incinerating of pasminco sand (34 wt.%), waste solvents and TDFs (both 80 wt.% reduction). Like PAHs, the presence of chlorine and potassium in tyres would naturally expect for it to catalyse PCDD/F generation, however as shown by other studies (Carrasco *et al.*, 2002; Trezza and Scian, 2009) the alkaline conditions of the PH/PC-kiln will enable the TDF to valorise and be encompassed within the clinker material. With sulfur being a natural component to conventional and most ADFs, its presence is shown to have a correlated inhibitor to the formation of PCDD/F through a correlated depletion of chlorine. As shown in subchapter 5.1.4, SO$_x$ UMEF during the co-incineration of pasminco sand, waste solvents and TDF showed many samples to be consistent with (or slightly above) baseline levels. Where samples were elevated (regardless of conventional or ADF use), the subsequent PCDD/F UMEF and HCl UMEF was shown to be particularly lower than other samples, or even undetectable (i.e. at LOD).
This is particularly noticeable for samples A6, A7, C5, C6, C7, E9, E10, E11, F1, F2, F4, F9, G1 to G9, H4 to H9, and I3 to I11. Experiential results published by Karstensen (2008a) further supports this, showing the circulation of PCDD/Fs are influenced by chlorides in the kiln and preheater, and respectively suppressed by a high sulfur concentration.

The regression analysis of PCDD$_{ex}$ emissions (Figure 7.4) for all kilns shows a correlation with the design and operations, namely the preheater material temperature, kiln fuel calorific value, kiln fuel rate, kiln flame residence time, kiln gas temperature and fuel-air ratio. The monitoring of these process parameters will identify when PCDD/F forming characteristics become more predominate, particularly when the alternative fuel properties (e.g. CV, initial temperature) are known. A comprehensive review by Altarawneh et al. (2009) on the homogenous pathways of PCDD/F formation, chlorination, and destruction identified that key operational influences include temperature, oxygen content and residence time.

![Figure 7.4: Regressional model of total PCDD$_{ex}$ UMEF.](image)

As the gas temperature window also plays a significant role to PCDD/F formation, it is important for the preheater’s upper cyclone stage to have a counter-flowing gas temperature >350 °C. This is required to maintain a consistent preheater material temperature for initial pyro-processing while achieving the appropriate residence time.
Several studies (Chen et al., 2016; Li et al., 2016) of PCDD/Fs only in the gas phase showed that similar concentrations were recorded the first and second preheater cyclones, however the PCDF ratio had largely increased (by 28 vol.%) through reforming and presence of H₂0 vapour. This will instigate ideal situations for surface-catalytic reactions when high volumes of gas have an abundance of particles. In comparison to the particle phase of flue gas, the studies also showed a decrease in PCDD concentrations between the two locations, with an increasing PCDD/F ratio (due to the presence of a chlorine donor). From the preheater cyclones, it is equally important for the quick cooling of flue gas to be achieved so the APCD is maintained below 200 °C, therefore being outside of the PCDD/F-forming gas temperature window of 200-450 °C. Results from Li et al. (2016) indicate a 4-fold increase in PCDD/F gas-phase concentrations post-APCD as opposed to a 2-fold increase in its particle-phase.

From the statistical analysis and plotting of PCDD_ex emissions, it is shown that most baseline and ADF trial samples have a strong standard of variance with the following calculated model of:

$$PCDD_{ex} = 0.0000000072 + 0.0000000011*K_f - 0.0000000058*PC_f + 0.0000000044*ADF_{gf} - 0.0000000088*K_{gf} - 0.0000000059*PC_{gf} + 0.0000000049*ADF_{ht} - 0.0000000033*Feed - 0.0000000004*Load - 0.0000000076*K_{ht} - 0.0000000011*K_{fr} - 0.0000000061*Load_{int} + 0.00000000093*PH_{gt} + 0.0000000012*PH_{int} + 0.0000000028*PH_{fr} - 0.0000000056*PC_{gt} + 0.0000000017*PC_{int} + 0.0000000058*PC_{fr} + 0.0000000012*K_{gt} + 0.0000000032*K_{ht} - 0.0000000023*K_{fr} - 0.0000000018*Air_f + 0.0000000094*S_1 - 0.046*O_e - 0.0000000013*H₂O + 0.0000000018*O₂ - 0.0000000022*CO₂$$

However, most these PCDD_ex results are somewhat different to the regressional analysis for halides and halogens (subchapter 5.1.6), which is shown to be primarily impacted with the rate of meal feed, clinker production and PH/PC gas temperatures. This indifference identifies the predominate PCDD/F forming mechanisms to be De Novo Synthesis, and this is further supported by each samples’ PCDD/F ratio as shown in Appendix 2. Other experiments (Altarawneh et al., 2009; Chen et al., 2014; Xhrouet et al., 2001) which co-incinerated at the precalciner showed similar results, but reported PCDF congeners to have a greater concentration than PCDD congeners. It is, however, also shown in Figure 7.3, that samples with the co-incineration of wood-waste and plastic (Plants D and E) and with tyres (Plants I and J), did correlate with an elevated chlorine and PCDD/F UMEF mostly due to a larger concentration of PCDD congeners. To act against the De Novo mechanism of chlorinated dioxins, preventative measures need to be in place so that APCD inlet
temperatures are maintained at below 250 °C (as noted by Karstensen, 2008b and 2009; Yan et al., 2014).

With an increasing amount of alternative fuel used amongst cement plants, waste oil showed no increase in PCDD/F UMEF (excluding sample A8) at a 3.5 ADF% 5.5 ADF% or 7.5 ADF%. The use of wood chips or TDF has also showed an incremental decrease in PCDD/F emissions, particularly with exchange of 25 ADF% and 19 ADF%, respectively. Nevertheless, it needs to be recognised that caution needs to be exercised in data interpretation as individual pollutant UMEF can vary over time and therefore any subsequent correlation will need to leverage off confidence in the sampling methodologies performed and stable operating conditions. CSI (2006) has shown the reporting of PCDD/F concentrations can vary dramatically during several hours (i.e. 0.05 to 4.3 ng I-TEQ m³) which were relevant to variability within the process conditions. An appropriate BMP to minimise this is the exclusion of co-incinerating ADF during start-up and shut down situations, and for its introduction to be during stabilized operations.

7.2.1 PCDD/F Nato ’95 I-TEQ

From the results of the PCDD/F samples, the standardising of an individual congeners significance (to the NATO ‘95 referenced I-TEQ of 2,3,7,8-TCDD) allows for the cross-examination of critical congener behaviors, and the cement kilns subsequent UMEF. Figure 7.5 shows the standardised UMEF values (referenced to NATO ’95 and WHO ‘05) which have some ADF trials concurrence to, or exceeding, the baseline fuel emission values. The exceeding values include all ADFs (excluding carbon dust), whereas the only significant low-carbon fuel to reduce PCDD/F I-TEQ values by 75 wt.% was TDFs.
Figure 7.5: Flue gas UMEF for PCDD-Nato_{ex} and PCDD-WHO_{ex} during baseline and ADF co-incineration.

Nevertheless, the emission monitoring results of PCDD-Nato_{ex} remain below the required international limit (including the EC (2000) Directive 2000/76/EC) of 0.1 ng I-TEQ/Nm³, along with the majority also being below (or close to) the report average 6.7x10⁻¹¹ kg PCDD/F UMEF for PH/PC-kiln plants in the USA (Marceau and VanGeem, 2011). Furthermore, most sample results also fall below the emission factor estimate presented by CSI (2006), with a PCDD I-TEQ UMEF of 0.037 µg/tonne (equivalent to 3.7 x 10⁻¹¹ kg/tonne) which is ¼ of the value used in the European inventory (van Loo, 2008). The statistical analysis of PCDD-Nato_{ex} UMEF values (Figure 7.6) shows a regresional correlation of key contributing parameters primarily to kiln’s ADF%, ADF firing rate, precalciner firing rate, rate of induced air, and the release amount of CO₂ and O₂ form the process. The calculated model for mass emission of PCDD-Nato_{ex} is:

\[
\text{PCDD-Nato}_{\text{ex}} = 0.00000000143 + 0.00000000027\times K_f - 0.00000000033\times PC_f + 0.00000000057\times ADF_{\text{gt}} - 0.00000000046\times K_{\text{gt}} - 0.00000000072\times PC_{\text{gt}} + 0.00000000051\times ADF_{\text{fr}} - 0.00000000053\times Feed - 0.00000000049\times \text{Load} - 0.00000000014\times K_f + 0.00000000001\times K_{\text{fr}} + 0.000000000084\times \text{Load}_{\text{gt}} + 0.00000000011\times PH_{\text{gt}} + 0.000000000028\times PH_{\text{fr}} + 0.000000000029\times PH_{\text{rt}} + 0.000000000086\times PC_{\text{gt}} - 0.000000000049\times PC_{\text{fr}} - 0.000000000031\times PC_{\text{rt}} + 0.000000000023\times K_{\text{gt}} - 0.000000000029\times K_{\text{fr}} + 0.000000000036\times K_{\text{rt}} - 0.000000000064\times Air_f - \]

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From the PCDD/F samples, the standardising of an individual congeners significance (to the WHO '05 referenced I-TEQ of 2,3,7,8-TCDD) shows the PCDD-WHOex emission values (Figure 7.5) to be similar with those standardised by the NATO '95 reference (PCDD-Natoex). It is shown that a consistent performance between most baseline operations and co-incineration is achieved while remaining below this established emission limit. Notable differences between samples include the co-incineration of wood chip and plastics yield an average increase of 260 wt.% increase to baseline values, whereas the use of TDF resulted in a PCDD-WHOex UMEF reduction 77 wt.%. Of course, several factors can influence the UMEF reduction during TDF co-incineration, particularly the availability of smaller particulate matter (including PM$_{10}$ and PM$_{2.5}$) or trace metalloids from its inert material and its subsequent need for removal from the selected APCD (being ESP-baghouse combination for Plant I and ESP-only for Plant J).

The regression analysis of PCDD-WHOex UMEF values (Figure 7.7) was also consistent with those described in the NATO '95 reference, except for ADF% substitute. The calculated model for PCDD-WHOex UMEF is:

\[
0.0000000000017*S_1 - 0.000000000015*O_e - 0.000000000019*H_2O + 0.000000000083*O_2 - 0.0000000000073*CO_2
\]
PCDD-WHO\textsubscript{ex} = 0.000000000143 + 0.00000000027*K\textsubscript{f} - 0.00000000033*PC\textsubscript{f} + 0.00000000057*ADF\% - 0.00000000046*K\textsubscript{fr} - 0.00000000072*PC\textsubscript{fr} + 0.00000000051*ADF\% - 0.000000000053*Feed - 0.00000000049*Load - 0.00000000014*K\textsubscript{fr} + 0.00000000001*K\textsubscript{fr} + 0.0000000000084*Load\textsubscript{mt} - 0.000000000011*PH\textsubscript{gt} + 0.000000000028*PH\textsubscript{mt} + 0.000000000029*PH\textsubscript{rt} + 0.0000000000086*PC\textsubscript{gt} - 0.000000000049*PC\textsubscript{mt} - 0.000000000031*PC\textsubscript{rt} + 0.00000000023*K\textsubscript{gt} - 0.000000000029*K\textsubscript{mt} + 0.00000000036*K\textsubscript{rt} - 0.000000000064*Air\textsubscript{f} - 0.00000000017*S\textsubscript{1} - 0.00000000015*O\textsubscript{2} - 0.00000000019*H\textsubscript{2}O + 0.00000000083*O\textsubscript{2} - 0.00000000073*CO\textsubscript{2}

**Figure 7.7:** Regressional model of PCDD-WHO\textsubscript{ex} UMEF.

The PCA score plot for PCDD-WHO\textsubscript{ex} shown in Figure 7.8 captured 78% variability of the monitoring dataset, and identifies most experimental samples to have a close profile to baseline UMEF results. However, the plotting of 4 wood chip samples (D9, F4, G4, H4), both RDF samples (D10, E10) and a TDF sample (J4) are shown to be located further apart due to divergent emission results. Given the high inert moisture and volatile content of these materials, these outlier values may be higher due to the proportionally effects of isolated blockages or lower temperatures (like Ariyaratne et al. (2013c)). However, this requires further investigation as other tests (such as Conesa et al., 2008) which co-incinerated wood chips (E9, H9) or shredded tyres (I4, I6, J8, J12) remained in close proximity to each other and with baseline UMEF results.
Figure 7.8: PCA score plot of UMEF of PCDD-WHO\textsubscript{ex} congeners from cement plants.

A profile of measured congener and homologue concentrations (Figure 7.9) is used to evaluate the distribution and identify those which have key contributions. From this, it is shown that some homologue groups account for most PCDD-WHO\textsubscript{ex} emissions during ADF runs. This is particularly noticeable with TCDD-F and PeCDD-F isomers (with percentage breakdown in brackets) being predominately accountable for 70\% toxicity for oil trials (30\%, 40\%) and wood chip trials (40\%, 30\%), and 90\% toxicity for waste solvent trials (55\%, 35\%). Co-incineration trials which measured furan concentrations, consistently showed toxicity contributions of <65\% from TCDD-F, PeCDD-F and HxCDD-F isomers.
Figure 7.9: Congener distribution of PCDD-WHO\textsubscript{ex} emissions obtained during ADF co-incineration.

As an important relationship to the presence of contaminants in cement plant emissions, the distribution and ratio of PCDD congeners to PCDF congeners measured under different cement plant conditions is shown in Figure 7.10. Normal plant operations show a relative proportion of PCDD/F ratios at 1:1, and ranging up to as much as 8:1 (e.g. samples A5, A6, B1, D5, E2, F5, G6, H5). As the dotted line in Figure 7.10 indicates an equal PCDD-PCDF proportion of the emissions, showing PCDD congeners (53 samples) to be more predominately than PCDD congeners (38 samples). Willitsch et al. (2003) supports this by noting the co-incineration within a cement plant does not contribute to a greater generation and distribution of PCDD congeners, primarily due to its high temperature, efficient mixing and complete destruction. Subsequent research published by Xhrouet et al. (2001), Chen et al. (2014) and Thuong et al. (2014) discount this by identifying total PCDF to have a greater concentration than total PCDD, with samples ranging up to a 1:28 ratio.

Explicitly with the co-incineration of waste oil, trail runs show to have a PCDF-dominating ratio in Plants B and C, but elevated PCDD concentrations were shown for Plant A. Given a similar concentration of chlorine amongst all baseline and ADF trails at these 3 cement plants, only Plant A was shown to have an effect of chlorinated PCDD/F
for both baseline and ADF tests. A key contributing factor for differences in contributing congeners is the type of flue gas treatment system used at each facility, whereby Plant A was fitted only with ESP, whereas Plants B and C both had a baghouse prior to its combined ESP unit.

![Figure 7.10: Total PCDD\textsubscript{ex} concentration and the ratio of PCDD to PCDF.](image)

The co-incineration of wood chips showed a PCDD-dominate ratio amongst all 6 samples which were used to varying ADF% rates and amongst 5 different plants. These results ranged between 1.5 to 5.7, and were considerably higher in PCDD congeners when referenced against its corresponding ratio from conventional combustion fuels. In contrast, the substitution of waste solvent has shown predominance to PCDF congeners, with samples F9 and G9 having a 1:5.8 and 1:2.9 ratio, respectively.

For the co-incineration of waste wood and plastic materials, the ratio of dioxins to furans congeners (shown in Figure 7.10) indicate a PCDD dominant ratio of 3.1:1 (sample D10) or a more-equal distribution and 1.3:1 ratio (sample E10). These results differ somewhat to other experimental trials with RDF (Chen et al., 2014; Zemba et al., 2011) which reported dominant contributions (of up to 95%) from lower chlorinated furans (HxCDF-TCDF). Similar to the key contributing factor noted above, plant D was fitted with two
ESPs, plant E used an ESP-baghouse combination, and trails performed by Chen et al. (2014) and Zemba et al. (2011) were at facilities which used baghouse filtration units. With the notion that ESPs support the formation of PCDD/Fs, experimental results show concentrations to be greater with the use of ESPs (6.5 µg/Sm³), than with an ESP-baghouse combination (2.3 µg/Sm³), or with baghouse-only treatment (1.4 µg/Sm³). Genon and Brizio (2008) further support this notion with the argument that the formation of PCDD/Fs derived from ADF would be only possible if the subsequent UMEF was decidedly higher to normal operations.

Relative to the fraction of 2,3,4,7,8-PeCDF to total mass emissions of I-TEQ PCDD/Fs, Figure 7.11 shows it not being the most abundant congener being released with the majority of baseline and experimental emissions being less than 35% vol. It is shown that the co-incineration of waste oil has shown a dominant presence of 2,3,4,7,8-PeCDF (between 30-42% vol.) whereas the co-incineration of wood chips or TDF showed a consistent and significantly less congener presence (<15% vol.), contrary to other studies by Conesa et al. (2011) and Karstensen (2008a).

**Figure 7.11:** Total PCDD/F I-TEQ concentration and its fraction of 2,3,4,7,8 PeCDF.
As detailed by Ishikawa and Herat (2012), the chlorination of organic material during co-incineration is somewhat scavenged by the alkaline PH/PC-kiln environment, and is less readily available for PCDD/F generation. As trace amounts of chlorine exist due to its inert concentration in raw meal and some conventional fuels used (e.g. coal), a surface area and catalytic metal compound for dioxin formation will also exist. Consistent with Genon and Brizio (2008), the lack of notable differences in the congener profiles of PCDD/Fs suggests that ADF co-incineration has a limiting influence and correlation to the essential conditions for De Novo or post-combustion formation (particularly to the 2,3,4,7,8-PeCDF congener), and the more effective control is the rate and environment of flue gas treatment and its thermal cooling window of 200 and 450 °C.

### 7.3 PCB and dl-PCB

The monitoring of PCB congeners has further identified the presence of dioxin-like compounds (dl-PCBs), which show a consistent UMEF value amongst numerous same-kiln runs, between differing kilns, with the use of conventional or alternative fuels, or with the increasing percentage substitution of ADF (Figure 7.12). With the substitution of waste oil, dl-PCB-WHOex UMEF values are shown to have no effect (or a slight improvement) to four of the six samples, with subtle increases recorded for samples B6 and C7 where the substitute firing rates were larger at 5.5% and 7.5%, respectively. The increased results were notably consistent with the hydrogen halide and total dl-PCBs measured values, and should be expected as its initial composition can include contain traces of metals and PCBs.
Figure 7.12: Flue gas total dl-PCB UMEF and dl-PCB-WHO\textsubscript{ex} UMEF during baseline and ADF co-incineration.

From the PCB samples, standardising individual congener’s significance (referenced to the WHO ‘05) has shown that all the trails (except samples E5 and I5) with an ADF\% substitute was at (or slightly above) the analytical LOD, and that the UMEF results for dl-PCB-WHO\textsubscript{ex} had an actual emission reduction (55 to 93 wt.\%) to baseline values. The results of increasing the percentage of wood chip substitute (samples D9, E9, F4, G4, H4) showed to have maintained a consistent UMEF reduction of 68 wt.\%, whereas the increased use of waste tyres to 14 wt.\% (J8) and 19 wt.\% (J12) had dl-PCB TEQ reductions of 87 wt.\% lower than baseline UMEF. The later tyre result is shown to be consistent with other co-incineration studies (Abad \textit{et al.}, 2004; Conesa \textit{et al.}, 2008) whereby the increase of thermal substitution rate with alternative fuels (sewage sludge and TDF, respectively) showed not direct effect on PCDD/F and PCB emissions. Figure 7.13 summarises the monitored UMEF results for PCDD-WHO\textsubscript{ex} and dl-PCB-WHO\textsubscript{ex}, showing the mean baseline rate (e.g. plant AA, BB, etc) on the left-hand side, and the experimental value (e.g. sample A4, A8, etc) and subsequent fuel type (e.g. oil, wood, RDF, tyres) positioned to the right-hand side.
Figure 7.13: PCDD-WHO\textsubscript{ex} and dl-PCB-WHO\textsubscript{ex} UMEF under baseline (conventional fuel) conditions or under co-incineration conditions.

However, a reduction to the mass emission of POPs congeners can only be of great significance if it impacts the distribution of health-critical PCDD/Fs and PCBs. Relative to the WHO (2005) dl-PCBs toxic criteria congeners, Figure 7.14 shows the dominant contributor to be PCB-126 (3,3',4,4',5-Pentachlorobiphenyl) throughout most ADF trials. Notable contributions of PCB-126 congeners are shown with the co-incineration of waste oil (by up to 50%, 70% and even 90%), solvents (both samples at 50%), wood chips (6 samples within 50-70%) and TDF (3 samples at 50%). For the release of PCB-169 (3,3',4,4',5,5'-Hexachlorobiphenyl) congeners, emission monitoring has shown smaller concentrations (between 10-25%) in ADF trials with waste oil, solvents, wood chips and TDF. Congener distribution of PCB-77 (3,3',4,4'-Tetrachlorobiphenyl) and PCB-81 (3,4,4',5-Tetrachlorobiphenyl) have shown to be primarily during the use of waste oil and TDF.
Figure 7.14: Congener distribution of dl-PCB-WHO\textsubscript{ex} emissions obtained during ADF co-incineration.

From this study, the emissions data collected has shown the waste co-incineration trials to be well below the EC Directive limits for PCDD/Fs (0.1 ng I-TEQ/Nm$^3$), and extremely below for PCBs (0.01 ng TEQ/Nm$^3$) irrespective of fuel mixture ratios. These findings are also found to be like other waste co-incineration publications (Abad et al., 2004; Conesa et al., 2008; Rovira et al., 2010; 30), whereby an increase in fuel thermal substitution does not necessarily correlate to an elevated concentration of PCDD/Fs or PCBs.

Contrary to studies published by Rivera-Austrui et al. (2010 and 2013) the unit mass release of dl-PCB-WHO\textsubscript{ex} were recorded as either proportional or greater than the PCDD-WHO\textsubscript{ex} UMEF, which is concerning that the quantification of these target pollutants may have previously been underestimated. Genon and Brizio (2008) support this with the notion of PCB concentrations possibly being at least a thousand times higher than PCDD/F, and may generate precursor micro-pollutants for dioxin formation. With this research, the elevated dl-PCB-WHO\textsubscript{ex} emissions of significance is those from the co-incineration of wastes for samples B6 (oil), E11 (carbon dust), G9 (solvent), I6 and J12 (both being of shredded vehicular tyres), and its compositional presence of hydrogen and chlorides.
Results from field monitoring were used to perform a PCA against PCDD-WHO$_{ex}$ and dl-PCB-WHO$_{ex}$ congeners, so to examine UMEF similarities between pollutant groups. The UMEF loading plot from baseline and alternative fuels (Figure 7.15) showed a correlated change (whether positive or negative) will most likely occur with health-critical dl-PCBs (namely PCB-126 and PCB-169) when another pollutant UMEF changes. The plot has identified a mixed grouping of PCDD/F and dl-PCB congeners (regardless of their WHO-referenced TEQ values), not allowing for the statistical segregation and determination of key influencing process factors. The PCA also showed a predominance from the 1,2,3,7,8-PeCDF and 1,2,3,4,7,8-HxCDF congeners, differing to studies noted above whereby the greatest influence was found from other isomers such as OCDD, 2,3,7,8-TCDF or 2,3,4,7,8-PeCDF.

![Figure 7.15: Loading plot for PCA of PCDD-WHO$_{ex}$ and dl-PCB-WHO$_{ex}$.

The statistical analysis of dl-PCB$_{ex}$ congeners (Figure 7.16) showed a regresional correlation with kiln operating parameters, specifically preheater gas temperature, precalciner gas and material temperatures, and kiln flame and material temperatures. The program also plotted the correlation of measured and predicted PCB$_{ex}$ emission values with the following calculated model:
PCB_{ex} = -0.0013 + 0.00000000005*K_f + 0.00000006*PC_f - 0.000000007*ADF_f - 0.000000016*K_{fr} + 0.00000004*PC_{fr} + 0.000000003*ADF_{fr} + 0.00000004*Load + 0.00000002*K_{ft} + 0.00000002*K_{fr} + 0.00000009*Load_{ext} + 0.000000009*PH_{gt} - 0.00000002*PH_{mt} + 0.00000005*PH_{rt} + 0.00000017*PC_{gt} + 0.00000017*PC_{mt} + 0.00000001*PC_{rt} - 0.000000012*K_{gt} + 0.00000058*K_{mt} + 0.000000012*K_{rt} - 0.000000001*K_{ft} + 0.00000002*K_{fr} + 0.00000006*PC_{fr} - 0.0000000000062*K_f + 0.000000000022*K_{fr} + 0.000000000027*PC_{fr} - 0.000000000018*ADF_{fr} + 0.0000000000003*Feed + 0.000000000022*Load - 0.0000000000049*K_{fr} + 0.000000000018*K_{ft} + 0.000000000017*Load_{ext} + 0.000000000007*PH_{gt} + 0.000000000026*PH_{mt} - 0.0000000000077*PH_{rt} - 0.0000000000074*PC_{gt} + 0.000000000001*PC_{mt} - 0.0000000000017*PC_{rt} - 0.000000000014*K_{gt} + 0.000000000003*K_{mt} + 0.000000000015*K_{rt} + 0.000000000012*Air_f - 0.0000000000021*S_1 + 0.000000000035*O_2 - 0.0000000000079*H_2O - 0.000000000022*O_2 + 0.000000000031*CO_2

Figure 7.16: Regressional model of total PCB UMEF.

From the results of the total PCB samples, the standardising of an individual congener’s significance (to the WHO ‘05 referenced I-TEQ TCDD) has shown (in Figure 7.12) that all the trails with ADF% substation was at the limit of detection, or slightly above. The regression analysis of PCB-WHO_{ex} emissions (Figure 7.17) provided a correlation with preheater residence time, precalciner gas temperature, kiln caloric value, and kiln flame temperatures, with the following program calculated model:

PCB-WHO_{ex} = -0.0000183 + 0.000000000062*K_f + 0.000000000026*PC_f - 0.000000000018*ADF_{fr} - 0.000000000017*Load_{ext} + 0.000000000007*PH_{gt} - 0.000000000026*PH_{mt} - 0.0000000000077*PH_{rt} - 0.0000000000074*PC_{gt} + 0.000000000001*PC_{mt} - 0.0000000000017*PC_{rt} - 0.000000000014*K_{gt} + 0.000000000003*K_{mt} + 0.000000000015*K_{rt} + 0.000000000012*Air_f - 0.0000000000021*S_1 + 0.000000000035*O_2 - 0.000000000079*H_2O - 0.000000000022*O_2 + 0.000000000031*CO_2

The UMEF dispersion for dl-PCB-WHO_{ex} are shown in Figure 7.18 in comparison to hydrogen halide (i.e. HF, HCl), total PCDD/F, and total dl-PCB values. As identified in subchapters 5.1.6 and 5.2.5, the regressional analysis of these compounds identified a
similar correlation with dl-PCB-WHO\textsubscript{ex} congeners on the key-contributing plant conditions, particularly with the preheater-precalciner gas temperatures and the kiln flame temperature.

**Figure 7.17**: Regressional model of PCB-WHO\textsubscript{ex} UMEF.

**Figure 7.18**: Box-plot of pollutant UMEF results.
Divergent to dioxins, the score plot for dl-PCB-WHO\textsubscript{ex} (Figure 7.19) with a 78% variability, showed no specific differences between baseline and experimental UMEF as each principle component had a similar cluster profile (with co-incineration results being amongst baseline emission results). This included those co-incineration tests (B6, E11, G9, I6, J12) previously noted with elevated emissions, with the major UMEF contribution to dl-PCB-WHO\textsubscript{ex} being from PCB-126 and PCB-169 (Figure 7.15). Like Rivera-Austrui et al. (2014), the use of RDF and TDF has indicated an emission predominance from the volatile, lighter non-ortho dl-PCBs (including PCB-77 and PCB-81) more-so to the heavier mono-ortho dl-PCBs.

**Figure 7.19**: PCA score plot of UMEF of dl-PCB-WHO\textsubscript{ex} congeners.

In summary, co-incineration of waste materials showed a correlating (or reduced) UMEF to PCDD-WHO\textsubscript{ex} and dl-PCB-WHO\textsubscript{ex} congeners with oil, pasminco sand, anode carbon dust, solvents and TDF. The co-incineration of waste-chips or RDF was shown to increase PCDD-WHO\textsubscript{ex} emissions, yet able to reduce dl-PCB-WHO\textsubscript{ex} emissions below baseline standards.
Chapter 8: Key operating conditions that influence optimised co-incineration

Waste co-incineration has been examined in chapters 5, 6 and 7 as they relate to the suppression and control of target pollutants, identifying key operating conditions which influences the individual and overall optimisation. The use of multivariate data analysis has shown that attention to these variables can support the suppression, and even its destruction, of air pollutants when attention is placed on the following key influential process parameters:

- Precalcer and kiln fuel firing rate and residence time;
- Preheater and precalcer gas and material temperature;
- Kiln flame temperature;
- Fuel-air ratio and percentage of excess oxygen; and
- Mass flow of meal feed and clinker loading.

Karstensen (2008a) supports this finding by highlight the most important element for cement manufacturing is to have sufficient temperature, oxygen, retention time, and proper mixing conditions. Under circumstances of temperature drop or fluctuations caused by a varying fuel firing rate, it is shown that certain process mechanisms will effectively alter its thermal conductivity and provide suitable conditions for pollutant formation and emission.

An assessment of these key operating conditions which influence pollutant-forming mechanisms is shown in Figure 8.1 for the PH, PC and kiln. Consistent with the results published by Cao et al. (2010), Figure 8.1a shows why the oxygen-fuel equivalence of >1% is necessary to ensure the PC co-incineration conditions remain favourable for the use of alternative fuels. Where the mixture ratio is below this S1 value, the absence of oxygen within the precalciner increases greatly, resulting in the plant being averse to the sustainable combustion of low-carbon fuels and adequate heat transfer. With relevance to excess O2 in the preheater cyclones (Figure 8.1b), measurements that exist outside of the optimal O2 range are shown to result in considerable heat loss along with the potential to generate additional pollutants such as PICs and NOx.
The simulation of partial fuel replacement in the precalciner (Figure 8.1c and Figure 8.1d) has shown an elevated material and gas temperature can permeate an increased fuel firing rate and residence time. Optimisation of kiln flame temperature is shown (Figure 8.1e) to greatest where the required residence time is sufficient to its reciprocal fuel firing rate. It is shown that where an inadequate or excessive amount of fuel being supplied to the burner, the combustion residence time will be considerably insufficient to achieve complete combustion and maintain the required flame temperature.
**Figure 8.1:** 3D surface graphs of key operating conditions that influence pollutant-forming mechanisms against (a) and (b) PH gas and material conditions; (c) and (d) PC gas and material conditions; (e) kiln firing rate and flame residence time.

Additional factors evaluated from the regresional modelling which were shown to somewhat contribute towards the suppression of pollutant emission, include:

- Amount of catalytic and carboneous material within the process and emitted as CO₂;
- Preheater and Precalciner residence time;
- Rate of induced air;
- Kiln fuel calorific value; and
- Kiln gas and material temperature.
Chapter 9: Most optimised alternative fuel for use in clinker production

A summary of the above results is shown in Table 9.1, collated to the relevant alternative fuels trialled. The table indicates the differential change (if any) of the air pollutant concentration against its respective kiln baseline emissions, but does not identify the magnitude of change. The indicators are representing no change of emission levels (●), and increase to emission levels due to ADF use (▲), and a decrease of emission levels due to ADF use (▼). The following subchapter reviews the effectiveness of materials to the overall emission performance; gaseous pollutant emissions; particulate and trace pollutant emission; and clinker production.

9.1 Effective ADF to Overall Emissions

Overall, the co-incineration trials using waste oil, carbon dust, waste solvents and TDF within differing cement kilns was shown to have the minimal influence on baseline emission rates, or had significantly reduced the concentration of emitted pollutant. Specific to the waste oil trials, the reported levels were significant lower than the baseline averages for TSP (24 wt.%), halogens (80 wt.%), TVOCs (32 wt.%), SOx (15 vol.%), BTX (75 wt.%), heavy metals (73 wt.%), and PCB-WHOex (72 wt.%).

For the carbon dust trials, the reported levels were less than the baseline average for CO (47 vol.%), PCDDex (80 wt.%), PCBex (36 wt.%), and PCB-WHOex (72 wt.%).

The co-incineration trials with waste solvents have reported lower emission levels to the baseline averages for TSP (33 wt.%), CO (40 vol.%), TVOC (31 wt.%), heavy metals (53 wt.%), PAH (90 wt.%), PAH BaPex (90 wt.%), PCDDex (80 wt.%), PCBex (49 wt.%), and PCB-WHOex (93 wt.%).

Lastly for TDF, the recorded emission levels were less than the baseline averages for TSP (52 wt.%), SOx (49 vol.%), PAH (90 wt.%), PAH BaPex (50 wt.%), PCDDex (80 wt.%), PCDD-Natoex (75 wt.%), PCDD-WHOex (75 wt.%), and PCB-WHOex (93 wt.%). The overall synthesis of pollutant contributions is shown to be analogous to Albino et al. (2011) with benefits to reducing industry GHG emissions, energy recovery and unnecessary incineration or landfill disposal, and the safe destruction of hazardous materials.
Table 9.1: Increase, decrease or no change to kiln emission concentrations with ADFs

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<td>I-TEQ NATO₆₆</td>
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<tr>
<td>Dioxin-like PCB₆₆</td>
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<td>PCB-TEQ WHO₆₆</td>
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As the different forms of waste require different handling arrangements and operating considerations, consideration to applicability and effectiveness of an effective alternative fuel needs to be fully understood. For example, this can include the particle size or viscosity of the fuel, its storage and handling, and its compatibility with existing infrastructure.

9.2 Effective ADF to Gaseous Pollutants

From the results, it is shown the co-incineration of waste oil, pasminco sand, wood chips, wood chips and plastic, waste solvents and TDF have a minimal influence, or had significantly reduced, the UMEF of gaseous pollutants when compared to baseline mass emission rates. This is particularly noticeable at varying ADF substitution rates, as well as between differing facilities. Carbon dioxide emissions were shown to be successfully co-incinerated with all fuel substitutes being comparable to (or below) normal emissions. Numerous tests on co-incinerating wood chips showed a 20 vol.% reduction against baseline CO\textsubscript{2} values. For the evaluation of other key pollutants relative to CO\textsubscript{2}’s GWP, Figure 9.1 shows the calculated CO\textsubscript{2}\textsubscript{e} value (per equation 2.6) for each respective sample against its in-field CO\textsubscript{2} measurement. This regresional analysis further supports the field measurements and findings presented for these contributing pollutants during the use of conventional and ADF co-incineration, showing a calculated model of:

\[
\text{CO}_2\text{e} = (0.0016\times\text{CO}_2 \text{ UMEF}) + 0.1077
\]  
\text{Equation 9.1}
Monitoring of CO also showed the use of most fuel substitutes (excluding waste oil) in clinker production was also comparable to (or below) normal emissions, with exceptionally reduced values during pasminco sand, wood chips, wood chips with plastics, and the co-incineration of carbon dust. Most baseline and co-incineration tests were shown to have NO\textsubscript{x} UMEF concurrent with reports of other European cement plant emissions, with some significant reductions particularly being with the use of wood chips and TDF. With sulfur being a naturally occurring compound to other carboneous fuels like coal, the use of low sulfur-containing substitutes showed (surprisingly) no considerable improvement to normal plant emissions. Whereas, a noticeable reduction to TVOC emissions was shown to occur predominantly with the co-incineration of waste oil, pasminco sand, wood chips with plastics, waste solvents and TDF.

9.3 Effective ADF to Particulate and Trace Pollutants

For particulates and trace species, the results identified the use of waste oil, waste solvents and TDF to have a more-predominate DRE of key pollutants, whilst providing the required energy demands. With the substitution of waste oils (at 3.5 wt.%, 5 wt.%, 5.5 wt.% and 7.5 wt.%), the overall results displayed consistent (or improved) UMEF for PM, metals, PAH and PCBs. For the substitution of pasminco sand, wood chips, and wood chips with 5-10 wt.% plastics; the monitoring results each identified consistent (or
improved) emissions with most metals. Increased concentrations were identified (similar to the use of waste oils) with BaP-TEQ PAHs and PCDD/F (including I-TEQ standards).

With the use of carbon dust, UMEF results had a consistent (or improved) correlation with PM, most metals, BaP-TEQ PAHs, PCDD/F (total and I-TEQ) and PCBs (total and I-TEQ). However, increased UMEF levels were identified with total PAHs. With the use of waste solvents, UMEF results had a consistent (or improved) emission with all target pollutants, except for increases to Cr\(^{3+}\) and I-TEQ referenced PCDD/Fs. With the use of TDF, UMEF results had a consistent (or improved) emission with particulates, some metals, PAH (total and I-TEQ), PCDD/F (total and I-TEQ) and I-TEQ PCBs. Concentration increases were identified for most metals (including Cr\(^{6+}\), Pb, Hg, Ni and Zn), and total PCBs. This is consistent with reputable studies Giannopoulos et al., 2007b; Herat, 1994; Batelle, 2002; ICF, 2008; Pipilikaki et al., 2005). Of interest to this paper, and supported by other studies, is the PCDD/F reducing effect through the co-incineration of waste tyres.

With the experimental undertaking, there are noticeable similarities identified on formation of particulate emissions (with certain ADFs) as with PAH, PCDD/F and PCB, CO\(_2\) and SO\(_x\) emissions. Lastly, “dioxin-like” PCB emissions were consistent with halide and halogen emissions, regardless of ADF type.

9.4 Effective to Production Rate

In assessing the impact to clinker production, an energy saving factor and annual clinker capacity was calculated for each ADF% as shown in Table 9.2. Where a consistent performance was possible upheld, most ADF samples are shown to have no impact to the Load (i.e. clinker production rate). From these, sample F9 shows the co-incineration of waste solvent (at 7 ADF%) is the only test to reduce the Load rate by 4 wt.%.

As the alternative fuel has a considerably LHV (Table 4.1), it could be expected that a subsequent increase in fuel firing rate or fuel mass load to sustain the same energy input may result in effects to the clinker production rate.

Comparatively, the co-incineration of wood chips, which also yields a relatively low heating value, does not display any adverse effects to the rate of clinker production. More so, it is shown that the use of wood chips has similar influences on clinker production rate as does TDF (which has a substantially higher LHV).
tests, it is shown that no impact to clinker production has occurred during the optimised co-incineration of an alternative fuel.

With these waste fuel types and at the rates of ADF%, it is shown that no impact to the cement production rate will primarily be achieved when key operating parameters are maintained to a baseline performance, and that the formation and quantification of key pollutants (e.g. moisture, ash, volatiles, alkali chlorides and sulfates, PCDD/F) are maintained accordingly so that process upsets (e.g. \( K_f, K_{ft}, K_g, O_e, S_i \)) and the circulation of blockages are prevented. This is particularly important where the waste fuel type has a high immersed moisture content which will require an increased residence time or flame temperature as more energy will be needed for its heating and evaporation. Furthermore, and similar to the conclusions drawn by El Atasi’s (2013) environmental impact assessment, UMEF reduction of CO\(_2\) (and other pollutants) is shown to be greatly influenced by the efficiency of the waste being equally burnt as with other carboneous fuels (i.e. DRE is at the greatest extent possible).

**Table 9.2:** Plant energy savings and clinker capacity with ADF co-incineration

<table>
<thead>
<tr>
<th>Sample Reference</th>
<th>Plant clinker rate (mtpa)</th>
<th>ADF type, ADF%</th>
<th>ADF co-incinerated</th>
<th>Clinker capacity with ADF% (mtpa)</th>
<th>Change (%)</th>
<th>Energy savings per mass clinker (MJ/tonne)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A4</td>
<td>0.65</td>
<td>Oil, 3.5</td>
<td>0.69</td>
<td>6</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>A8</td>
<td>0.65</td>
<td>Oil, 5.5</td>
<td>0.71</td>
<td>9</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>B3</td>
<td>0.53</td>
<td>Oil, 3.5</td>
<td>0.6</td>
<td>13</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>B6</td>
<td>0.53</td>
<td>Oil, 5.5</td>
<td>0.57</td>
<td>8</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>C4</td>
<td>0.51</td>
<td>Oil, 5</td>
<td>0.53</td>
<td>4</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>C7</td>
<td>0.51</td>
<td>Oil, 7.5</td>
<td>0.57</td>
<td>12</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>D8</td>
<td>0.94</td>
<td>Pasminco sand, 15</td>
<td>1.0</td>
<td>6</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>D9</td>
<td>0.94</td>
<td>Wood chips, 25</td>
<td>0.97</td>
<td>3</td>
<td>480</td>
<td></td>
</tr>
<tr>
<td>D10</td>
<td>0.94</td>
<td>Wood chips &amp; 5-10% plastics, 40</td>
<td>1.0</td>
<td>6</td>
<td>330</td>
<td></td>
</tr>
<tr>
<td>D11</td>
<td>0.94</td>
<td>Carbon dust, 10</td>
<td>0.95</td>
<td>1</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>E8</td>
<td>1.3</td>
<td>Pasminco sand, 15</td>
<td>1.4</td>
<td>8</td>
<td>330</td>
<td></td>
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</table>
The review of both clinker production rates and energy savings shows some similarities to general estimates presented by Price et al. (2009) and Hasanbeigi et al. (2012b), predominately with the use of wood and TDF. With a significant energy saving estimate of 600 MJ/tonne clinker, it may be largely overestimated with the above claim that all alternative fuel types will achieve these significant savings with no impact to the rate of clinker or any additional operating costs. Despite the inclusion of 5-10 wt.% plastics to wood chips, and therefore a higher CV, it is shown that no significant improvement to the clinker capacity rate will be achieved. This limitation will be largely due to amount of moisture content in the ADF, and the effects as described above. Furthermore and based on its inert compositions, RDF will also have a noticeably larger particle size than other carboneous fuels, subsequently inducing some of the key pollutants mentioned above (predominately ash and volatiles).

As detailed in Table 9.2 and Hasanbeigi et al. (2012b), more research is required to the potential energy saving and its correlated bottleneck to clinker production with other ADF types (e.g. biomass) and non-operating barriers (e.g. plant age, technical knowledge, capital investment costs). Conflicting to Ariyaratne et al. (2013c and 2014b), the co-incineration of ADF did not necessarily show a reduced production capacity (i.e.
bottleneck) based on its fuel type. With PH/PC-kiln characteristics shown to be maintained during co-incineration, existing facilities were capable to adapt and therefore not necessarily need to incorporate additional process techniques (e.g. oxygen enrichment). This in-turn will permit for the co-incineration of available and suitable waste types to be considered and incorporated into a waste hierarchy system. Here it is shown to have a significant effect to reducing waste disposal needs and costs while contributing to the energy efficiency demand of cement manufacturing while causing no considerable impact to its production capacity.
Chapter 10: Conclusion and recommendations for future work

As detailed in Chapter 1, the focus of this thesis has been to study the effects of co-incinerating different alternative derived fuels within several cement kilns operating under normal conditions. Several questions on optimised ADF co-incineration were identified so to gain a greater understanding, and emissions monitoring of experimental conditions were examined and further coupled with mathematical modelling.

10.1 Concluding Discussion

Cement manufacturing remains a significant sector to developed and non-developed countries, yet its contributions to CO$_2$ and other hazardous air pollutants remains of considerable concern. With economic growth and consumption patterns, an increasingly demand for clinker production will require a linear, and continuous, amount of heat and energy. It is shown through various studies that resource recovery can achieve reduced emissions to numerous pollutants (including CO$_2$), making the co-incinerating technology a preferred alternative for sound and safe waste disposal over incinerators and other non-scientific methods. Aligned with numerous global action strategies for pollution and production cost reductions, the acceptance and adoption of this well-documented technology needs to be capitalised by regulatory agencies in coordination with manufacturing facilities. This action requires to address the current regulatory barriers in place, and to address community concerns by invoking greater confidence in its use and by being more transparency in pollutant behaviour and subsequent destruction.

The focus of this study is to answer some key questions arising when co-incinerating alternative derived fuels in cement manufacturing while subsequently meeting, or reduce if possible, the current cement industry emission targets. Emissions monitoring and analytical modeling of flue gas from 10 cement plants have been performed with some new information presented on the performance of co-incinerating waste materials within PH/PC-kilns. For the 7 derived waste fuels used in the trials, the obligations specifically related to the reduction of material to landfill, the safe destruction of hazardous wastes, the cost savings of waste handling, and other benefits which relate to reducing conventional fuel extraction. Each PC/PH kiln presented the typical requirements for hazardous waste incineration, namely very high core and combustion temperatures, extended fuel-flame residence time, gas turbulence, stoichiometric mixing, thermal
inertia, existing post-combustion pollutant techniques and no waste residual for further disposal. To some extent, the five research questions from subchapter 1.3.1 can be answered.

1. What are the impacts on CO$_2$ and other air pollutants UMEF?

The tests performed have indicated the use of waste oil, pasminco sand, wood chips, wood chips and plastic (RDF), waste solvents and TDFs are favourable in sustaining (or reducing) target gaseous emissions values to normal operations, whilst providing the required energy demands for clinker production. As a heterogeneous fuel by its inherent nature, the use of RDF materials still requires representative sampling and characterisation to prepare process conditions and evaluate expected pollutant UMEFs. The impact to CO$_2$ were shown to be successful, with the co-incineration of selected fuel substitutes resulting in a comparable UMEF. The use of wood chips particularly showed a significant 20 vol.% reduction against baseline CO$_2$ values. Other gaseous pollutants (such as CO, NOx and TVOCs) were shown to also shown a comparable (or reduced) emission to baseline values.

Similarly, the co-incineration trials of waste oil, waste solvents and TDF within differing cement kilns were shown to have minimal (or a significantly-reduced) influence on particulate and trace elements when compared to baseline results. Particulate matter (including PM$_{10}$ and PM$_{2.5}$) were only shown to be most improved with waste oils, solvents and TDF, whereas most heavy metals were shown to have similar (or improved) emissions with the co-incineration of all alternative fuel types. Specific to PCDD-F and dl-PCB I-TEQ congers, the co-incineration of waste oil, pasminco sand, anode carbon dust, solvents and TDF is shown to be integrated into an existing system and provide the necessary fuel for combustion and calcination, while achieving the required 99.9999% destructive removal efficiency and remaining below the EC Directive limit of 0.1 ng I-TEQ/Nm$^3$. However, it was shown the co-incineration of waste-chips or RDF increased PCDD-WHO$_{ex}$ emissions, yet able to reduce dl-PCB-WHO$_{ex}$ emissions to baseline conditions. The distribution of TCDD/F and PeCDD/F isomers (as PCDD/F toxicity) was found to be dominate in the use of oil, wood chips, and solvents, while the distribution of PCB-126 (as dl-PCB toxicity) was also accounted during these trials and with TDF.

From the thesis, it is shown the formation of dioxins in cement production facility does not necessarily depend on the compositional constituents of the ADF co-incinerated (i.e.
chlorine-containing fuels), and that other process parameters (such as preheater material temperature, kiln fuel calorific value, kiln flame residence time, kiln gas temperature) can influence PCDD/F unit mass emissions. This concept is further supported by Rahman et al. (2012 and 2013) studies whereby no individual fuel type can claim to be the best, and giving the suggestion to quantify of ADF blends (e.g. like wood chips with 5-10 wt.% plastics) so to maximise co-incinerations’ optimisation.

2. What emission rates are affected by an increased amount of substituted fuel?
The co-incineration of an increasing ADF%, was conducted with several fuel types either within the same facility or amongst differing plants, showing minor subsequent effects to emission factors will occur and that the key process parameters contribute to contaminant suppression and destruction. Varying ratios of waste oil co-incineration showed no change to CO₂ and PCDD/F emissions, whereas an increase in TDF substitution rates showed a corresponding increase to its CO₂ UMEF. Monitoring results for cement plant J (with TDF) identified the generation of CO to be proportionally increased with the ADF% substitution, whereas NOₓ UMEF showed a correlating reduction to baseline emissions by up to 43 vol.% and well below average European cement plant levels.

With an increased substitution rate of wood chips, the formation of PCDD congeners were shown to be considerably higher when referenced against its corresponding conventional fuel, whereas the increased use of waste solvent can result in PCDF congeners to be a more dominate. Monitoring of dl-PCBs (standardized to WHO ’05) values were shown to have no effect (or some improvement) with increased firing rates at varying facilities with waste oil or wood chip substitute. Regardless of the amount of fuel substituted, it is shown that for samples conducted under varying ADF percentages that a consistent supply of raw meal will create a uniform and continuous gas-material mixing condition, alleviating for the generation of unburnt fuel, uncalcinated meal, CO and other pollutants.

3. Which fuel properties influence combustion characteristics and pollutant-forming mechanisms?
In general, PH/PC-kiln emissions are shown to be site-specific with some variances between facilities, making it challenging to identify influential properties and mechanism. Furthermore, as the chemical and physical properties of waste materials are going to differ
amongst themselves and to conventional carbeneous fuels, the completeness of combustion is going to vary greatly with much dependence on the kinetics of the reactions which are undergone. From this thesis, the main effects of fuel characteristics which influence pollutant-forming mechanisms, and subsequently clinker production rate, are best illustrated in **Figure 10.1**.

**Figure 10.1**: Summary of fuel properties that influence pollutant-forming mechanisms.

With considerations to clinker quality and production rate, experiential tests have shown fuels of a larger carbon content or particle size to be more influential to pollutant formation and emission than those with a smaller CV (e.g. wood chips, waste solvents). Where heating and devolisation of fuels require a greater $S_1$, it is shown that additional reducing agents like volatiles, alkali chlorides, CO, or TSP can form from unburnt carbon, which may deposit downstream and cause possible build-ups if not operationally controlled. Co-incineration is also shown to have a minor influence on heavy metals UMEF, except where Hg may be present and therefore the highly volatile compounds are released into the flue gas emissions.
Where substitute materials have a high carbon-hydrogen composition, the increased generation and release of CO\textsubscript{2} and CO from co-incineration will be evident where stoichiometric conditions are not achieved. Immersed moisture (or water content) of an alternative fuel is shown to influence flame temperature, flame residence time, and unnecessary increases to the fuel firing rate which is shown to increase the formation of PICs and fuel NO\textsubscript{x} as well as the need for a longer meal-gas residence time. Lastly, the co-incinerating chloride-containing fuels (e.g. waste oil, plastic, TDF) has shown some variations within each kiln run as well as some subtle increases to its respective chlorine UMEF (expressed as HCl) primarily due to higher gas temperatures and its ability for later condensation.

4. Which key operating parameters are impacted from fuel substitution, and what fuel properties influence these effects?

As with many industrial countries, the acceptance to utilise existing cement kilns to co-process general or hazardous waste has been instigated for decades, and the degree of its utilisation is constantly increasing to adapt to global CO\textsubscript{2} emission reduction goals. The experimental tests of this research have shown that today’s cement kilns (under normal operating conditions and present pollution control techniques) can suppress the formation of GHG and air pollutants, when attention is placed on the following key influential process parameters:

- Precalciner and kiln fuel firing rate and residence time;
- Preheater and precalciner gas and material temperature;
- Kiln flame temperature and residence time;
- Fuel-air ratio and percentage of excess oxygen; and
- Mass flow of meal feed and clinker loading.

Additional factors which somewhat contributed to the suppression of specific gaseous and air toxic emissions include:

- Amount of catalytic and carboneous material within the process and emitted as CO\textsubscript{2};
- Preheater and Precalciner residence time;
- Rate of induced air;
- Kiln fuel calorific value; and
- Kiln gas and material temperature.

This research has shown the above various techniques and inputs are viable for suppressing the formation of GHG and air toxics, and has produced empirical models for the formation and eventual emission of pollutants. For the consideration of cost-effectiveness, the additional monitoring of these variables is minimal as key influencing process parameters exist within most of today's cement manufacturing kilns. Each PC/PH kiln presented the typical requirements for hazardous waste incineration, namely very high core and combustion temperatures, extended fuel-flame residence time, gas turbulence, stoichiometric mixing, thermal inertia, existing post-combustion pollutant techniques and no waste residual for further disposal. It is shown that increasing the fuel firing rate during co-incineration is of significance so to maintain PH/PC-kiln gas and material temperatures, and the mass balance of \( S_1 \), \( O_6 \) and exhaust gas.

5. What are the impacts to the rate of clinker production, and are any bottlenecks formed?

Waste co-incineration is shown to contribute to the efficiency of used energy while causing no considerable impact to the clinker production rate (Table 9.2) or operating costs. An important component to this is that key operating parameters need to be maintained to its respective baseline conditions so that absent pollutant-forming mechanisms are not introduced, and so that process upsets or blockages are inadvertently prevented. Additional attention may be required if a waste fuel has a high moisture content as more energy will be needed for its heating and evaporation. Where a fuel has a low heating value, it is shown that the need for a higher fuel firing rate or mass loading will not necessary imply a reduction to the plant’s production capacity. This thesis also shows similar influences on the clinker production rate can be achieved even with ADFs of differing LHV's (e.g. wood chips and TDF).

When applied locally with available and suitable waste types, co-incineration should have a function within the waste hierarchy system, as it is shown numerous times to have a significant effect to reduce waste generation and disposal needs, sub sequential relief on human and environmental health impacts, reduces hazardous waste disposal costs, while providing business with cost-savings and the manufacturing industry with competition. These economic incentives provide industry with flexibilities and opportunities, and encourage the technological innovations needed to meet air quality goals along with the
co-incineration of alternative waste fuels. This integrated approach serves a useful solution in providing a fuel or other means to generate energy, while conserving natural resources, in line with the Basel Convention Annex 4B notation that an operation which may lead to resource recovery, recycling reclamation, direct re-use or alternative uses (UNEP, 2012).

10.2 Contribution to Knowledge

Contribution of knowledge from the works has shown the actualized reduction of gaseous and particulate pollutants during the co-incineration of alternative fuels, with some of the following additional attributes:

- field experiments captured the successive effects from co-incineration of varying alternative fuels which are abundant and readily available. The selective use of these are an important consideration that contributes towards climate change targets and beyond;
- modelling has shown the co-incineration of ADF will not sequentially result in negative impacts to the clinker production rate, and that waste types of differing heating values (e.g. woods chips and TDF) are shown to have similar influences (or lack of) to normal operations. Critical to this outcome is the formation and quantification of key pollutants that inhibit process upsets and the circulation of blockages; and considerations of the above may be evaluated for use in future cement plant designs to incorporate waste co-incineration to an optimal standard of production, essentially supporting the regulatory and local community acceptance with its use;
- key operating parameters have demonstrated their impacts to baseline UMEF, the degree of cause-and-effect to certain catalysts (e.g. presence of chloride) and subsequent pollutant inhibitors (e.g. fuel firing rate, $S_1$, rate of induced air);

10.3 Avenues and Recommendations for Further Work

Recognising the importance and diversity of cement production within society, and with the above evidence that optimised co-incineration of alternative waste materials can be
achieved, the following are some additional areas whereby suggested areas of further research can be undertaken.

10.3.1 Optimised co-incineration

Some additional information on optimising alternative fuels co-incineration of alternative fuels can improved the knowledge gap with the following attributes:

1. Examine CO₂ and hazardous air pollutants UMEF during the co-incineration of other readily-available ADF types (e.g. biomass) that’s lacks available published literature.
2. It is observed that other sorting methodologies to plastic-containing wastes (e.g. RFD) can be examined so to reduce the immersed moisture content and shredded particle size.
3. Further examine the impacts of an increased ADF firing rate at the secondary burner (while maintaining its stoichiometric flame temperature and O₂ content for thermal NOₓ formation). This could be with the same experiential fuels used in this thesis, or other readily-available materials as mentioned above.
4. Examine the impacts of other non-operating barriers (e.g. plant age, capital investment costs) towards co-incineration.

Regardless of slight variations in plant operations, meal or fuel composition or clinker product, further experimental trials could be performed on additional waste streams not identified, particularly on hazardous waste types. Like this thesis, and as noted in Akkapeddi (2008), the preparation and alteration of an existing PH/PC-kiln is timely, however it is necessary for the plant to consistently maintain its operating parameters whilst undergoing experimental fuel-substitute trials. This is reinforced through other publications whereby the establishment of a program is necessary so to minimise lag times between baseline and experimental burn times, and to also utilise more than one plant for a comparative, unbiased analysis. Future experimental trials should also consider undertaking several incremental ADF% rates (recommend a minimum of 3), as this provides an additional variable to assess to pollutant formation and emission. Of importance to the assessment is maintaining a consistent mass flow of meal feed and clinker loading.
10.3.2 ADF% substitution rate and clinker production

Within this thesis differing rates of convention fuel substitution for various other materials was shown, however additional knowledge may be gain by further investigations to the following:

1. Examine the impacts (both emissions and production capacity) of increasing the firing rate of secondary fuel, and combining this with an increasing ADF%.

2. Examine an improved form of preparing and handling alternative waste materials so that the ADF firing rate at the secondary burner can be greatly increased (subsequently increasing the ADF%) and the possibility of co-incinerating ADF more at the kiln primary burner.

In general, the impacts to different PH/PC-kiln systems is not completely examined or understood. Subchapter 9.4 of this thesis details important ADF factors on clinker production rate, of which can be validated further by:

1. Assessing the impact to production capacity through the co-incineration of a specific ADF (e.g. waste oil, wood chips, solvents, TDF) across varying sized PH/PC-kilns as this will allow for greater examination. It may be advantageous to have triplicate samples performed at a single facility for correlating its impact.

2. Examine the impacts to production rate with other alternative waste types discussed in subchapter 10.3.1, and the subsequent impacts of increasing its ADFr and ADF%.
References


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Appendix 1: CO₂ theoretical emission factor

For the manufacturing of cement, theoretical emission factor (EF) for CO₂ generation is the combination of fuel combustion (EF<sub>fc</sub>) and clinker produced (EF<sub>cp</sub>), as mathematically used through the following equations (Stefanović <i>et al.</i>, 2010).

For fuel combustion:

\[
\text{CO}_2 \text{ EF}_{fc} = (\text{EF}_{ab} + \text{EF}_{ab}) \ast \text{Load} \ast D_y \tag{A-1}
\]

where \(a\) is the fuel type, and \(b\) is the sector of fuel source,

- \(\text{Load}\) is average clinker production rate (t/day),
- \(D_y\) is number of days operating per year.

\[
\text{EF}_{ab} = \frac{44}{12} \ast \text{C}_\text{C fuel} \tag{A-2}
\]

where \(\text{C}_\text{C fuel}\) is the fuel carbon content to oxidise

For clinker produced:

\[
\text{CO}_2 \text{ EF}_{cp} = \text{EF}_{cl} \ast \text{Load} \ast D_y \tag{A-3}
\]

where \(\text{EF}_{cl}\) is the CO₂ emission factor for produced clinker (t/t)<sup>19</sup>

\[
\text{EF}_{cl} = \frac{44}{56.1} \ast \text{CaO} + \frac{44}{40.3} \ast \text{MgO} \tag{A-4}
\]

Given, complete calcination of typical limestone, the \(\text{EF}_{cl}\) is between 0.52 and 0.55 tonnes CO₂ per tonne of clinker. Therefore, the total CO₂ emission factor from cement manufacturing (CO₂ EF) per year is:

\[
\text{CO}_2 \text{ EF} = \text{EF}_{fc} + \text{EF}_{cp} \tag{A-5}
\]

Relative to the cement plant facility, the specific emission (CO₂ SE) for CO₂ per tonne of clinker produced, is:

\[
\text{CO}_2 \text{ SE} = \frac{\text{CO}_2 \text{ EF}}{\text{Load} \ast D_y} \tag{A-6}
\]

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<sup>19</sup> Based on all CaO and MgO is removed from inert material, releasing all CO₂
Appendix 2: Cement plant operating parameters during sampling and resulting UMEF