Air emission from the co-combustion of alternative derived fuels within cement plants: Gaseous pollutants

Glen Richards and Igor E. Agranovski*

School of Engineering, Griffith University, Brisbane, Queensland, Australia

*Please address correspondence to: Igor E. Agranovski, Griffith School of Engineering, Griffith University, Brisbane 4111, QLD, Australia; e-mail: i.agranovski@griffith.edu.au

Cement manufacturing is a resource- and energy-intensive industry, utilizing 9% of global industrial energy use while releasing more than 5% of global carbon dioxide (CO₂) emissions. With an increasing demand of production set to double by 2050, so too will be its carbon footprint. However, Australian cement plants have great potential for energy savings and emission reductions through the substitution of combustion fuels with a proportion of alternative derived fuels (ADFs), namely, fuels derived from wastes. This paper presents the environmental emissions monitoring of 10 cement batching plants while under baseline and ADF operating conditions, and an assessment of parameters influencing combustion. The experiential runs included the varied substitution rates of seven waste streams and the monitoring of seven target pollutants. The co-combustion tests of waste oil, wood chips, wood chips and plastic, waste solvents, and shredded tires were shown to have the minimal influence when compared to baseline runs, or had significantly reduced the unit mass emission factor of pollutants. With an increasing ADF% substitution, monitoring identified there to be no subsequent emission effects and that key process parameters contributing to contaminant suppression include (1) precalciner and kiln fuel firing rate and residence time; (2) preheater and precalciner gas and material temperature; (3) rotary kiln flame temperature; (4) fuel–air ratio and percentage of excess oxygen; and (5) the rate of meal feed and rate of clinker produced.

Implications: Monitoring of gaseous air emission from 10 rotary kilns used in cement industry showed that full compliance to site and international obligations can be achieved while providing the required energy demands. Benefits specifically related to reduction of materials to landfill, safe destruction of hazardous wastes, cost savings of waste handling, and reduction of fossil fuel extraction are achievable and look promising from both environmental and economic perspectives.

Introduction

The brisk increase of global industrialization and development in recent decades has called for a similar demand for the production of cement. As a fundamental ingredient, the global production rate of cement has increased from 0.58 billion tonnes (1970) to 3.1 billion tonnes (2010), and is forecast to peak at 6.1 billion tonnes (2050) (Cembureau, 2010; Cement Sustainability Initiative [CSI], 2012; Holcim-GTZ, 2011).

As cement is considered the second most consumed material worldwide, and its manufacture is a resource- and energy-intensive industry, it currently demands 9% of industrial energy use and is accountable for 5% of carbon dioxide (CO₂) emissions (International Energy Agency [IEA], 2007). Localized CO₂ emission levels can be more extensive in developing countries; for example, 57% of China’s CO₂ emissions is from cement production (Lei et al., 2011).

In manufacturing cement clinker, the process involves crushing and blending of minerals as raw meal, which is later chemically transformed into clinker through staged intensive heating. Two key pollutant-generating components of this process are the release of bonded CO₂ from the calcination of limestone and magnesium carbonate, and the combustion of fuel for electricity and process needs (Cement Industry Foundation [CIF], 2005; European Integrated Pollution Prevention and Control Bureau [EIPPCB], 2011).

Under normal stoichiometric conditions of combustion, the generation of pollutants would be minimal. However, with the use of various fuels and materials, the realistic emanation from cement manufacturing is the product of incomplete combustion, and/or by-products of particulate and gaseous contaminants. The gaseous contaminants of specific interest to this paper include CO₂, carbon monoxide (CO), nitrogen oxides (NOₓ, expressed as NO₂), sulfur oxides (SOₓ, expressed as H₂SO₄), hydrogen halides and halogens, and total volatile organic compounds (TVOCs). The formation, suspension, control, and release of these contaminants largely depend on various components, including fuel composition, process design and operation, and combustion conditions.

As the endothermic reactions to produce a tonne of cement equally release the same amount of CO₂ into the atmosphere (referred as unit mass emission factor [UMEF]), the amounts of future emissions from cement manufacturing are set to double by 2050 (IEA, 2007; EIPPCB, 2011; U.S. Environmental Protection...
Reports by the Intergovernmental Panel on Climate Change (IPCC) identify that the 450-ppmv CO$_2$ limit target will only be achieved if current trends of energy consumption and UMEF are reduced by 50–80% (2000 equivalent CO$_2$ levels) by 2050 (IPCC, 2007). Furthermore, the release of these key gaseous pollutants can also have a health impact to the living organisms, including humans.

Various international case studies have shown the cement industry has the highest potential energy savings of 24%, primarily through the combustion of hazardous waste and partial substitution of alternative derived fuels (ADFs) (IEA, 2007; Bhatty et al., 2011; IEA, 2010). The co-combustion of ADFs within cement plants is not only a viable option for a reduction to fossil fuel consumption and CO$_2$ emissions reduction. It also provides a more environmentally sound disposal option and recovery of energy from the current operations of conventional incinerators (Bhatty et al., 2011; Cembureau, 2009; Conesa et al., 2008; Schneider et al., 2011).

Regardless of these results (Baier, 2006; Karstensen et al., 2005; Pipilikaki et al., 2005; Schneider et al., 2011), contrasting viewpoints from industry and government in Australia ultimately contribute to the current substitution within cement plants being only at 6 ADF% (World Business Council for Sustainable Development [WBCSD], 2010). There are, however, examples within Europe whereby the average substitution rate within cement plants is at 18 ADF%, with nine countries currently exceeding 25 ADF% (Cembureau, 2010; WBCSD, 2010; European Commission [EC], 2000). Standing alone, the Netherlands display an extraordinary example toward environmental sound management, as fuel substitution within cement plants is currently exceeding 83 ADF% (Cembureau, 2010).

Cement manufacturing involves the mechanical grinding and blending of raw materials into a meal of constituents, which is then transferred into a preheater/precalciner (PH/PC) tower and kiln system (Figure 1) for staged combustion and calcination. For the PH/PC tower, the preheater is a series of interconnecting cyclones and ducts, designed for the initial drying of immersed moisture, oxidizing organic compounds, calcination of limestone and magnesium carbonate, and centrifugal heating of the raw meal up to 750°C.

The precalciner vessel is positioned prior to the rotary kiln, and has the provisions of secondary fuel and combustion gases (referred to as tertiary air) at 21% oxygen (O$_2$) (Neuffer et al., 2007). As this fuel does not need to be of quality equal to the kiln burner, the predominate secondary fuel used here is coal. As this stage utilizes 60–70% of the total fuel for achieving

![Figure 1. Process design of PH/PC kiln system.](image_url)
95% calcination, the greatest opportunity to supplement the process with ADFs (even of lower calorific content) is within the precalciner (e.g., EIPPCB, 2011; Karstensen et al., 2005).

From the precalciner, the feed material is moved into a brick-lined rotary kiln. With slow revolutions, the material travels the kiln length, where it undergoes final sintering into clinker (Cembureau, 2009; Neuffer et al., 2007). As cement kilns are complex, the near-complete destruction of pollutants is greatly derived by numerous variables such as fuel calorific value (CV), combustion gas and meal temperatures, heat loss, residence time, fuel and meal compositions, excess air, moisture content, and turbulence (Boubel et al., 1994).

The clinker leaves the kiln combustion zone and enters the cooler, where it is cooled with induced air, and continues for later blending, grinding, storage, and shipment. Waste heat is recovered and redirected from the cooler into the kiln (as secondary air) or as combustion air in the precalciner (as tertiary air). Once this hot countercflowing flue gas has passed the preheater tower, it is directed through the selected pollutant control devices (either fabric filters or electrostatic precipitators) and exits the emission stack.

Under normal conditions, the exothermic oxidation of fossil fuels and air to produce heat and thermal energy requires an equal balance of time, temperature, and turbulence. Within material combustion, there are four main components (Mokrzycki et al., 2003) that are important for the transfer of thermal energy transfer from combustion to a heat load, including:

1. The transfer of heat from the flame (greatly affected by the fuel load).
2. The burner, which oxidizes the combustible fuel to release the heat.
3. The kiln sintering and combustion zones for appropriate residence time.
4. The heat recovery device, which influences the thermal efficiency of the system.

As the efficient mixing of fuel and air in a turbulent form is significant, complete combustion requires this to be at the flame; otherwise, it will have to be oxidized downstream at hotspots. Where the fuel type or feed rate is not constant, dead spots are created, which can lead to the formation of particulates and gaseous pollutants. Furthermore, the stoichiometric amount of oxygen (at a mixture equivalent ratio with fuel) must be sustainable so that it doesn’t become rich (O2 deficient) or lean (excess O2) (Mycock et al., 1995). Cement plants generally operate with leaner amounts of air, however this needs to be minimal in order to reduce heat loss and NOx emissions.

With the majority of cement plants within Australia, natural gas or powderized coal is ultimately utilized at the secondary fuel feed location in the precalciner vessel. As fuel composition can vary from time to time and place to place, this can have a subsequent effect on the process chemical and physical behavior.

This research aims to demonstrate that while operating under normal conditions, the factors that influence the formation of gaseous pollutants during co-processing ADFs are minimal when compared to the baseline emission levels. Similar to other ADF trials (Baier, 2006; Karstensen et al., 2005, Pipilikaki et al., 2005), this research is to objectively demonstrate that the release of cement manufacturing pollutants remains below generally imposed limits, and that complete destruction and irreversible transformation are achieved (Karstensen et al., 2005). Further, for gaseous pollutants, a consecutive companion paper will extend the research into the formation and monitoring of particulate emissions (including total solid particulates, heavy metals, dioxins, and furans) during the co-combustion of ADFs within cement plants.

**Materials and Methodology**

**Materials**

Analytical monitoring of flue gas from 10 cement batching plants (referenced A, B, C, up to J) was selected while they were actively operating with traditional fuels (collected as baseline emissions) or with the partial substitution of ADF only at the precalciner secondary fuel location (collected as experimental emissions). Sequential monitoring of these emission runs was numbered further for each plant, such as A1, A2, A3, through to A8 for cement plant A. For baseline emissions monitoring, at a minimum three runs were conducted on the stack sampling ports of each rotary kiln, with the systems’ operating condition being considered as the average of the sampling duration.

For ADF emissions monitoring, each experimental run was simulated to the respective plants’ baseline runs, with all fuels being thoroughly mixed prior to use. In total, 94 baseline and experimental runs were sampled and monitored. The fuels used for the experimental runs included waste oils (an even mixture of cutting fluids and road vehicle engines), Pasmico black sand, wood chips, wood chips and 5–10% plastics, carbon dust (from alumina smelter anode formers), waste solvents, and shredded vehicular tire-derived fuels (TDF).

Table 1 summarizes these fuels’ general composition, CV, and percentage of ADF substitution. The percentage of fuel substitution over various test included waste oil at 3.5–7.5 ADF%, Pasmico black sand at 15 ADF%, wood chips at 7–25 ADF%, wood chips and plastics at 40 ADF%, carbon dust at 10 ADF%, and TDF at 5.5–19 ADF%.

During the undertaking of each sample run, 26 plant operating parameters were recorded, including the fuel type and calorific values; ADF% substitution; fuel and ADF% firing rate; rate of meal feed and clinker produced; process areas’ gas/material mean temperatures and residence times; fuel–air ratio (S1); percent excess air, and flue gas conditions.

**Monitoring methodology**

For the monitoring of gaseous emissions during the production of clinker, the following isokinetic and continuous standards were complied with. Sampling access to the process flue gas was via four 6-inch flanged ports located at the top of the emission stack (seen in Figure 1).
Isokinetic sampling. For isokinetic sampling, source gas is withdrawn through the sharp-tapered nozzle of a heated sampling train at a controlled flow rate so to provide an accurate and representative sample. For efficient isokinetcity, the nozzle is positioned in parallel with the flue gas flow direction along numerous traverse points, per EPA Method 1 (EPA, 1983a), and the sample velocity at the nozzle inlet is altered to mirror the approaching stack gas velocity and any nearby flow disturbances.

Stack gas velocity, temperature, and volumetric flow rate were measured with a Stausseheibe (S-type) Pitot, a thermocouple, and a differential pressure gauge per EPA Method 2 (EPA, 1983b). A series of chilled Greenberg–Smith impingers with condenser or reagents is used to remove water vapor or target pollutants (e.g., SOx, HCl, HF), respectively. The gas moisture content was calculated per EPA Method 4 (EPA, 1983c), allowing for the determination of dry gas molecular weight per EPA Method 3 (EPA, 1990).

The sampling for sulfur oxides was performed in accordance with EPA Method 8 (EPA, 1977), where a measured volume of stack gas is withdrawn isokinetically through an impinger of 80% isopropanol (used to remove SO3 and H2SO4), a glass fiber filter, and a final impinger of 3% hydrogen peroxide (for the collection of SO2). The aqueous solutions and filter were analyzed by the barium–thorin titration method for the concentration of SO2, SO3, and H2SO4.

Sampling of hydrogen halides and halogens is in accordance with EPA Method 26A (EPA, 1994a) where a known gas volume is isokinetically withdrawn through a heated probe and filter (later discarded), and condensed into two impingers of 0.1 molar sulfuric acid and two impingers of dilute sodium hydroxide (with sodium thiosulfate added postsampling). The hydrogen halides were solubilized in the acidic solution and form chloride and fluoride ions. The halogens have a very low solubility in the acidic solution and pass through for collection.

---

**Table 1. Summary of ADF characteristics for experimental tests**

| ADF type                  | ADF composition (%) | CV (MJ/kg) | ADF sample reference | ADF% substitution |
|---------------------------|---------------------|------------|----------------------|-------------------|
| Waste oil                 |                     | 17 to 30   |                      |                   |
| Carbon (70%)              |                     | A4         | 3.5                  |
| Hydrogen (15%)            |                     | A8         | 5.5                  |
| Moisture (10%)            |                     | B3         | 3.5                  |
| Sulfur (1%)               |                     | B6         | 5.5                  |
| Halogens (1%)             |                     | C4         | 5                    |
| VOCs (1%)                 |                     | C7         | 7.5                  |
| Pasmico black sand        | Carbon (70%)        | 25 to 27   |                      |                   |
| Hydrogen (15%)            |                     | E8         | 15                   |
| Moisture (10%)            |                     |           |                      |                   |
| Wood chips                | Carbon (60–75%)     | 14 to 18   |                      |                   |
| Hydrogen (6%)             |                     | D9         | 25                   |
| Moisture (2%)             |                     | E9         | 25                   |
| Sulfur (2%)               |                     | F4         | 10                   |
| Wood chips and 5–10% plastics | Carbon (45–70%)  | 26 to 27   |                      |                   |
| Hydrogen (4%)             |                     | D10        | 40                   |
| Moisture (2%)             |                     | E10        | 40                   |
| Halogens (1%)             |                     |           |                      |                   |
| VOCs (1%)                 |                     |           |                      |                   |
| Carbon dust               | Carbon (80%)        | 25         |                      |                   |
| Sulfur (2%)               |                     | D11        | 10                   |
| Waste solvents            | Carbon (30%)        | 18 to 21   |                      |                   |
| Hydrogen (20%)            |                     | F9         | 7                    |
| PAH (6%)                  |                     | G9         | 7                    |
| VOCs (1%)                 |                     |           |                      |                   |
| TDF                       | Carbon (70–85%)     | 24 to 30   |                      |                   |
| Hydrogen (5–8%)           |                     | I4         | 5.5                  |
| Moisture (1%)             |                     | I6         | 8.1                  |
| Sulfur (1%)               |                     | J4         | 7.6                  |
| Halogens (0.5%)           |                     | J8         | 14                   |
| Metals (5%)               |                     | J12        | 19                   |

**Notes:** PAH, polycyclic aromatic hydrocarbon, VOCs, volatile organic compounds.
to the alkaline solution. Halide ions and halogens were measured from the aqueous solutions by ion chromatography, and the acid gases are later expressed as hydrogen chloride (HCl) and hydrogen fluoride (HF).

Sampling and analysis for TVOCs is conducted in accordance with EPA Method 18 (EPA, 1994b) where a measured volume of gas is drawn through a series of impingers (for condensate) and then an activated carbon tube (for trapping TVOCs). Afterward, the tube samples were extracted with carbon disulfide and analyzed with a gas chromatograph, and the results were later correlated to an n-hexane standard.

Once sampled, the flue gas measurements were used to calculate the normalized flow rate at 0°C temperature and 1 atm pressure. Over the duration of the sampling, changes in the required isokinetic flow rate at each traverse point create variation in the samples’ true representation. Verification of each sample’s overall isokinetcity percentage (%I) was calculated post test (to within 100%I ± 10%), signifying the samples accuracy and validation.

Continuous sampling. Monitoring of O2, CO, CO2, NO, and NO2 was conducted and recorded with a Testo 350XL portable multigas emissions analyzer (calibrated to certain certified span gases and zeroed with ultrahigh-purity [UHP] nitrogen). Sample gas was withdrawn continuously from the stack sampling port into the analyzer, where O2 and CO2 were monitored per EPA Method 3A (EPA, 2006) through a paramagnetic O2 analyzer (serial 01133471) and a nondispersive infrared (NDIR) CO2 analyzer (serial 01008558). Carbon monoxide was monitored per EPA Method 10 (EPA, 2008) through an NDIR CO analyzer (serial 01025427), and nitrogen oxides were monitored per EPA Method 7E (EPA, 1986) through an NO/NO2/NOx chemiluminescent analyzer (serial 01138341).

Modeling methodology. The examination of multivariate data is to signify the degree of influence from parameters of pollutant formation, kinetics, and suppression during the co-combustion of ADFs. The use of a statistical computer package Unscrambler X (developed by Camo) allows for the generation of empirical models (by partial least squares) and normalizing key emission-influencing variables (by principle component analysis). From the isokinetic and continuous monitoring techniques conducted, the UMEF (kg/tonne) was calculated on the pollutants’ mass emission rate per unit of clinker produced. This UMEF was modeled 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 modeling components of X–Y loading and of weighted regressional coefficient.

Results

For a correlation on key operating parameters consistency across different batching plants, 11 parameters were noticeably constant and included the PH/PC and kiln chamber (gas and material temperatures, and retention times), and the kiln flame (temperature and time). Figure 2 displays the mean and nominal variance of the remaining parameters, where it can be seen that each of these (regardless of plant size or production rate) still remains relative with other operating plants.

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. Monitoring of CO2 gas within the exhaust stream will vary based on the level of calcination and the complete combustion of the carbonous fuel. For the 94 samples, the majority of CO2 UMEF results are observed to be relatively constant within plants (Figure 3). In this and other figures, baseline samples are represented with circle markers and ADF samples with diamond markers. With the substitution trials of waste oil, Pasmico black sand, wood chips with plastics, and carbon

Figure 2. Calibration of cement plant key operating conditions.

Figure 3. Mass CO2 emitted per clinker tonne under baseline and ADF conditions.
dust (in cement plants A to E), the CO$_2$ UMEF was either consistent or below the respective average baseline results.

Given that these fuels have a high carbon–hydrogen composition, the increased generation and release of CO$_2$ from ADF use would be evident in the event that stoichiometric conditions were not achieved. The suppression of CO$_2$ (of up to 30%) is further supported as the calorific value 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 values were either consistent or slightly above average baseline results. Of all the ADF types trialed, TDFs have the largest CV and carbon content, which would have been expected to have the most improved CO$_2$ emissions. This result has been subsequently influenced by the plants’ lean stoichiometric ratio, extending between 108 and 113%.

With comparison of Figure 3 to the estimated 534 kg CO$_2$ UMEF published in the National Inventory Report 2011 (Department of Industry, Innovation, Climate Change, Science, Research and Tertiary Education [DIICCSRTE], 2011) or the European estimated 672 kg CO$_2$ UMEF (EIPPCB, 2011), the mean values of all tests for each cement plant were either considerably above (plants E, I, J) or below these referenced figures. With the exception of TDFs, all ADF runs were either aligned or below this referenced estimate.

The regresional analysis of CO$_2$ UMEF (Figure 4) showed great linearity between operating parameters, baseline or ADF runs, and modeling of predicted values. The modeling of CO$_2$ UMEF showed a strong regresional relationship with the ADF firing rate, PH/PC gas and material temperatures, meal feed rate, and clinker produced. As the loading rate of meal and fuel into the system is an important component for clinker production, the effects of CO$_2$ UMEF can be heavily influence by the balance of ADF use and the achievement of calcination temperatures with the PH/PC tower.

The CO UMEF results presented in Figure 5 show the baseline levels to be relatively consistent in some cement plants (namely, A, B, and H) and inconsistent within others. However, the use of all ADFs (excluding waste oil) has shown a sustained or reduced CO UMEF to baseline averages, specifically with Pasmico black sand (64%), wood chips (40%), wood chips with plastics (50%), and carbon dust (65%). Comparing them to the European reported emission levels of 0.46 kg CO UMEF (EIPPCB, 2011), the majority of baseline and ADF samples fall below this value. Furthermore, with the analysis of CO formation and emission, there is a comparative similarity to the CO$_2$ UMEF values sampled.

Similarly to carbon dioxide, the statistical modeling of CO UMEF (Figure 6) showed a consistent correlation with CO$_2$ and O$_2$, as well as the PH/PC gas and material temperatures, material retention time, meal feed rate, and clinker produced. This correlation is further supported as the air–fuel ratio was stoichiometric to lean (at 1.0 to 1.4) during all plant runs (baseline and ADF). With the substitution of ADFs that have a lower CV of baseline fuels

Figure 4. Predicted vs. measured concentration values for CO$_2$.

Figure 5. Mass CO emitted per clinker tonne under baseline and ADF conditions.
(and therefore require less $O_2$), complete combustion is more readily able to occur and subsequently the 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 an emission reduction to baseline values of up to 46% and 70%, respectively. However, the comparative use of TDF ($CV = 24–30$ MJ/kg) showed only one positive test result (sample J4), even with a stoichiometric air–fuel ratio.

The results of NO$_x$ UMEF (Figure 7) showed 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 NO$_x$ UMEF (EIPPCB, 2011), the majority of baseline and ADF samples are concurrently within this range. The use of waste oil at 3.5, 5.5, and 7.5 ADF% substitutions has shown a release of baseline NO$_x$ UMEF results, and a correlating effect with CO$_2$ UMEF (Figure 3) and CO UMEF (Figure 5) values. The use of waste wood has shown an NO$_x$ reduction of up to 90% of baseline values, while waste solvents results have an increase (of 20%) compare to differing plants’ baseline results.

With the substitution of TDF, four NO$_x$ UMEF results showed a decrease to baseline sampling of up to 43%. One result (sample J4) has shown an outstanding increase to baseline NO$_x$ levels by 80%; however, this sample also correlates to one substantially low CO level of 45% below baseline. The regresional analysis of NO$_x$ UMEF (Figure 8) showed a correlation with thermal NO$_x$ formation (primarily due to precalciner and kiln residence time, excess air, and S1) and prompt NO$_x$ (from residual water concentration).

The monitoring of SO$_x$ UMEF under baseline conditions has shown cement plants (A, C, and E to I) operating with emission fluctuations (Figure 9). As the cement plants utilize coal at the secondary fuel location, the presence of SO$_x$ is evident in baseline runs. With the substitution of an ADF with a lower sulfur content (including waste oil, Pasmico black sand, solvents, and tires), the SO$_x$ UMEF has showed the majority of samples to be consistent with (or slightly above) baseline levels, similar to that defined by other studies.

With the 40% fuel substitution of general waste (with 5–10% plastics) and wood chips, there is limited evidence of increased SO$_x$ UMEF results when referenced against 15% fuel substitution of wood chips or against baseline emissions. The regresional analysis on the formation of SO$_x$ pollutants (Figure 10) showed a strong correlation with the precalciner firing rate, average meal feed and clinker produced, excess air, and S1.

The monitoring of fluorides identified a minor presence of compounds within the flue gas, with this being predominately undetected in most cement plants and among all fuel types (Figure 11). These results also align with European cement emission reports of $2.3$ g/t HF UMEF (EIPPCB, 2011). For plant J, the samples did display some presence of fluorides; however, the use of ADF was shown to have a decreased emission level, by 15%. The sample monitoring of HCl within cement emissions (Figure 12) has shown some variations.

![Figure 6. Predicted vs. measured concentration values for CO.](image)

![Figure 7. Mass NO$_x$ emitted per clinker tonne under baseline and ADF conditions.](image)
within each kiln run, with similar ADF trials in differing plants and among various fuel types.

The monitoring did, however, show that the combustion of wood chips with plastics and of tires did increase chlorine emissions (by 26% and 89%, respectively), as supported by other studies. Furthermore, the increased substitution in ADF% also increased the chlorine emissions accordingly (e.g., plant H and plant J). The statistical analysis of hydrogen halides and halogens showed a regresional correlation primarily with the average meal feed and clinker produced, kiln flame and gas temperature, PH/PC gas temperatures, and S1.

Monitoring of TVOC UMEF are shown to have some variation within cement plants and between differing fuel type runs. Figure 13 displays the impartial influence of TVOC generation through the co-combustion of low-carbon ADFs (15% average reduction) when compared to normal operations. The decrease includes the use and increasing
ADF% of waste oil (33%), Pasmico black sand (76%), wood chips with plastics (21%), waste solvents (31%), and TDF (18%). In comparison to the European TVOC emission estimate of 0.002–0.13 kg TVOC UMEF (EIPPCB, 2011), the baseline and ADF samples are sustained within this range. The regressive modeling of TVOC UMEF (Figure 14) 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.

In summary, the co-combustion trials of waste oil, wood chips, wood chips and plastic, waste solvents, and TDF within differing cement kilns were shown to have minimal influence when compared to baseline emission rates, or significantly reduced the unit mass emission factor of gaseous pollutants.

**Discussion and Conclusion**

With the increasing demand for the production of cement being evident, its subsequent manufacture also demands large amounts of heat and energy. With availability, the utilization of typical fuels for combustion in the cement industry continues to emit various forms of gaseous and particulate pollutants; however, there have been strong improvements and acceptance in recent decades.

Analytical monitoring of flue gas from 10 cement plants was conducted while operating with traditional fuels (baseline) or with the partial substitution of ADF (experimental) at the precalciner. The target pollutants monitored or sampled during these runs included CO₂, CO, NOₓ, SOₓ, hydrogen halides and halogens, and TVOCs. For the seven alternative fuels tested, unit mass emission results have indicated the uses of waste oil, wood chips, wood chips and plastic, waste solvents, and TDFs are favorable in sustaining (or reducing) target emissions values to normal operations, while providing the required energy demands for clinker production.

The experimental test of ADF used in today’s cement kilns, under normal operating conditions, can suppress the formation of gaseous emissions, with particular attention to the following influential process parameters:

- Precalciner and kiln fuel firing rate and residence time.
- Preheater and precalciner gas and material temperature.
- Kiln flame temperature.
- Fuel–air ratio (S1) and percentage of excess oxygen.
- Average rate of meal feed rate and rate of clinker produced.

For the consideration of cost-effectiveness, the additional monitoring of these variables is minimal as the process parameters exist within most cement manufacturing kilns. The economic incentives provide industry with flexibilities and opportunities, and encourage the technological innovations needed to meet air quality goals along with the co-processing of alternative derived fuels.
Supplemental Material

Supplemental data for this article can be accessed at http://dx.doi.org/10.1080/10962247.2014.984084.

References

Baier, K. 2006. Solid replacement fuels (SRF) for use in co-incineration plants. ZKG International. Bauverlag, Gütersloh 59(3): 78–85.

Baukal, C. 2000. Heat Transfer in Industrial Combustion. Boca Raton, FL: CRC.

Bhatty, J, F. Miller, S. Kosmatka, and R., Bohan. 2011. Innovation in Portland Cement Manufacturing, Volume 2. Washington, DC: Portland Cement Association.

Boube, R., D. Fox, D. Turner, and A. Stern. 1994. Fundamentals of Air Pollution, 3rd ed. San Diego, CA: Academic Press.

Cembureau. 2009. Sustainable Cement Production: Co-Processing of Alternative Fuels and Raw Materials in the European Cement Industry. Brussels, Belgium: Cembureau.

Cembureau. 2010. Activity Report 2010. Brussels, Belgium: Cembureau.

Cement Industry Foundation. 2005. Cementing Our Future 2005-2030. Technology pathway for the Australian cement industry. Manuka, Australia: Cement Industry Federation.

Cement Sustainability Initiative. 2012. The Cement Sustainability Initiative: 10 Years of Progress—Moving on to the Next Decade. Geneva, Switzerland: World Business Council for Sustainable Development.

Conesa, J., A. Gálvez, F. Mateos, I. Martín-Gullón, and R. Font. 2008. Organic and inorganic pollutants from cement kiln stack feeding alternative fuels. J. Hazard. Mater. 158(2–3): 585–92. doi:10.1016/j.jhazmat.2008.01.116

Department of Industry, Innovation, Climate Change, Science, Research and Tertiary Education. 2013. Australian National Greenhouse Accounts—National Inventory Report 2011. Canberra, Australia: Australian Government.

ECOFYS. 2009. Methodology for the Free Allocation of Emission Allowances in the EU ETS Post 2012—Sector Report for the Cement Industry. Freiburg, Germany: European Commission, Oeko-Institut.

European Commission. 2000. Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the Incineration of Waste (L332). Off. J. Eur. Union L332: 91–111.

European Integrated Pollution Prevention and Control Bureau. 2011. Reference Document on the Best Available in the Cement, Lime and Magnesium Oxide Manufacturing Industries. Seville, Spain: European Commission, Institute for Prospective Technological Studies.

Holcim-GTZ. 2011. Draft Technical Guidelines on Co-processing of Hazardous Waste in Cement Kilns. Muttenz, Switzerland: University of Applied Sciences Northwestern Switzerland.

International Energy Agency. 2007. Tracking Industry Energy Efficiency and CO2 Emissions. Paris, France: International Energy Agency.

International Energy Agency. 2010. Cement Technology Roadmap 2009: Carbon emissions reductions up to 2050. Paris, France: International Energy Agency.

International Panel on Climate Change. 2007. Climate Change 2007: Mitigation of Climate Change. Cambridge, UK: Cambridge University Press.

Karstensen, K., N. Kinh, L. Thang, P. Viet, N. Tuan, D. Toi, N. Hung, T. Quan, D. Hanh, and D. Thang. 2005. Treatment of Organic Hazardous Waste in Vietnam—Test Burn in a Cement Kiln. Muttenz, Switzerland: University of Applied Sciences Northwestern Switzerland.

Lei, Y., Q. Zhang, C. Nielsen, and K. He. 2011. An inventory of primary air pollutants and CO2 emissions from cement production in China, 1990–2020. Atmos. Environ. 45:147–54. doi:10.1016/j.atmosenv.2010.09.034c

Mokrzycki, E., and A. Uliasz-Bohenczyk. 2003. Alternative fuels for the cement industry. Appl. Energy 74:95–100. doi:10.1016/S0306-2619(02)00135-6

Mycock, J., J. McKenna, and L. Theodore. 1995. Handbook of Air Pollution Control Engineering and Technology. Boca Raton, FL: CRC Press.

Neuffer, B., and B. Laney. 2007. Alternative Control Techniques Document Update—NOx Emissions from New Cement Kilns (EPA-453/R-07-006). Research Triangle Park, NC: U.S. EPA.

Pipilikaki, P., M. Katsioti, D. Papageorgiou, D. Fragoulis, and E. Chaniotakis. 2005. Use of tire derived fuel in clinker burning. Cement Concrete Composites 27:843–47. doi:10.1016/j.cemconcomp.2005.03.009

Schneider, M., M. Romer, M. Tschudin, and H. Bolio. 2011. Sustainable cement Production—Present and future. Cement Concrete Res. 41: 642–50. doi:10.1016/j.cemconres.2011.03.019

U.S. Environmental Protection Agency. 1977. Method 8—Determination of sulfuric acid mist & sulfur dioxide emissions from stationary sources. Fed. Reg. 41.754. http://www.epa.gov/ttnemc01/promgate/m-08.pdf (accessed December 12, 2014).

U.S. Environmental Protection Agency. 1983a. Method 1—Sample and velocity traverses for stationary sources. Fed. Reg. 45.034. http://www.epa.gov/ttnemc01/promgate/m-01.pdf (accessed December 12, 2014).

U.S. Environmental Protection Agency. 1983b. Method 2—Determination of stack gas velocity and volume flowrate (type S Pitot tube). Fed. Reg. 37.592. http://www.epa.gov/ttnemc01/promgate/m-02.pdf (accessed December 12, 2014).
U.S. Environmental Protection Agency. 1983c. Method 4—Determination of moisture content in stack gases. *Fed. Reg.* 55670. http://www.epa.gov/ttnemc01/promgate/m-04.pdf (accessed December 12, 2014).

U.S. Environmental Protection Agency. 1986. Method 7e—Determination of nitrogen oxides emissions from stationary sources (instrumental analyzer procedure). *Fed. Reg.* 21164. http://www.epa.gov/ttnemc01/promgate/m-07c.pdf (accessed December 12, 2014).

U.S. Environmental Protection Agency. 1990. Method 3—Gas analysis for the determination of dry molecular weight. *Fed. Reg.* 05211. http://www.epa.gov/ttnemc01/promgate/m-03.pdf (accessed December 12, 2014).

U.S. Environmental Protection Agency. 1994a. Method 26a—Determination of hydrogen halide and halogen emissions from stationary sources—Isokinetic method. *Fed. Reg.* 19309. http://www.epa.gov/ttnemc01/promgate/m-26a.pdf (accessed December 12, 2014).

U.S. Environmental Protection Agency. 1994b. Method 18—Measurement of gaseous organic compound emissions by gas chromatography—Adsorption tube procedure. *Fed. Reg.* 19308. http://www.epa.gov/ttnemc01/promgate/m-18.pdf (accessed December 12, 2014).

U.S. Environmental Protection Agency. 2006. Method 3a—Determination of oxygen and carbon dioxide concentrations in emissions from stationary sources (instrumental analyzer procedure). *Fed. Reg.* 28082. http://www.epa.gov/ttn/emc/promgate/m-03a.pdf (accessed December 12, 2014).

U.S. Environmental Protection Agency. 2008. Method 10—Determination of carbon monoxide emissions from stationary sources (instrumental analyzer procedure). *Fed. Reg.* 29691. http://www.epa.gov/ttn/emc/promgate/method10r06.pdf (accessed December 12, 2014).

U.S. Environmental Protection Agency. 2010. *Regulatory Impact Analysis: Amendments to the National Emission Standards for Hazardous Air Pollutants and New Source Performance Standards (NSPS) for Portland Cement Manufacturing Industry—Final Report.* Research Triangle Park, NC: Office of Air Quality Planning and Standards.

World Business Council for Sustainable Development. 2010. *Vision 2050: The New Agenda for Business.* Geneva, Switzerland: World Business Council for Sustainable Development.

**About the Authors**

Glen Richards is a regulatory & compliance manager at Bechtel Corporation, Perth Western Australia, Australia.

Igor E. Agranovski is a professor at the School of Engineering, Griffith University, Brisbane, Queensland, Australia.