Abstract

The manufacture of Portland cement is an energy intensive process. It produces significant pollution and uses large amounts on non-renewable resources. With increasing pressures to reduce greenhouse gas emissions due to cement manufacture, research and development of fuel alternatives and their effect on the manufacturing process has become an industry focus. The inherent properties of sintering cement in a rotary kiln allows for a large number of fuels to be burnt which are normally prohibited for use as fuel in other processes. To examine the suitability of a fuel, process modeling and simulation can be undertaken to predict the final impact of that fuel on kiln performance and greenhouse gas emission. With an accurate model and sufficient data, it is possible to conduct simulations for a wider range of alternative fuels. This paper discusses and summarizes the simulation results of three alternative fuels, namely spent carbon lining, used industrial lubricants and used tires, for identifying the most effective fuel source among these three. Among the selected fuels used, industrial lubricant is found to be the best option regarding the CO$_2$ emission, while the spent carbon lining is the worst one. In contrast, feed material requirements can be reduced by up to approximately 15% by using spent carbon lining. Further research is recommended to justify the findings.

Keywords: Cement; kiln; alternative fuels; process modelling; energy efficiency.

1. Introduction

Portland cement is one of the most commonly used construction materials in the world. The manufacture of Portland cement is energy intensive, requiring temperatures between 1450$^\circ$C and 1500$^\circ$C [1]. The manufacture of Portland cement accounts for approximately 5% of the annual carbon dioxide output. Half of these emissions originate from the burning of fuel and half from the calcination reactions [2]. Due to increasing pressures to implement sustainable and environmentally friendly manufacturing techniques, there has been increased exploration of alternative fuels to power the cement kiln. Testing of possible alternative fuels has been limited by the economic risks associated with real world experimentation with alternative fuels.

Modern Portland cement manufacturing technique was invented in 1824 [3] and, since the move to rotary kilns, very little has changed. As this process has been used for a long period of time, the chemical processes are well understood. The difficulty in modeling the process comes from the number of variables and reactions which take place. Attempting to model every possible reaction is well beyond the scope of this study and would require more specific process data than is available. For the purposes of this study, only a limited range of possible reactions have been considered. The reactions selected for consideration were those responsible for producing the four most prevalent products Alite, Belite, Calcium Aluminate and Ferrite.

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The main process routes for the manufacturing of cement vary with respect to equipment design, method of operation and fuel consumption [4]. The cement manufacturing process basically includes quarry, raw material preparation, preheating of raw material, kiln, clinker cooling, grinding, storage and dispatch. A schematic diagram of the cement manufacturing process is shown in figure 1 [5]. The process begins with decomposition of calcium carbonate (CaCO₃) at about 900°C to leave calcium oxide (CaO, lime) and liberate CO₂; this process is known as calcination. Then the clinkering process takes place in the kiln in which the calcium oxide reacts at high temperature (typically 1400°–1500°C) with silica, alumina and ferrous oxide to form the silicates, aluminates and ferrites respectively which make up the clinker. This clinker is cooled and then ground together with gypsum and other additives to produce cement.

To generate the required thermal energy, fuels are burnt in the kiln as well as in the preheater tower. The rotary kiln used in cement manufacturing is able to burn a wide range of materials due to the long residence time at high temperatures, the intrinsic ability for clinker to absorb and lock contaminants into the clinker and the alkalinity of the kiln environment. Materials like waste lubricants, plastics, used tires and sewage sludge are often proposed as alternative fuels for the cement industry. Meat and bone meal is also considered now as an alternative fuel [6]. Several agricultural biomass and industrial wastes are newly identified as potential alternative fuels for the cement industry. Spent carbon lining, an industrial waste of aluminium smelters, is one of the prospective alternative fuel candidates [7].

![Fig. 1. Schematic presentation of the cement manufacturing process from quarry to dispatch](image)

In order to reduce the risks of trialing a new alternative fuel, this study used a computer process model to predict the effects of selected alternative fuels on kiln performance and CO₂ emissions. These preliminary predictions will allow a larger range of fuels to be tested with minimal cost. Various commercial software packages are available to model and simulate the physical and chemical changes in industrial production. Thermodynamic models are extensively used in chemical and process engineering, materials technology as well as in energy and environmental technology. Most of the studies on modeling cement manufacturing found in the literature are based on computational fluid dynamics (CFD) [8-13]. Kaantee et al. [6] and Zhang et al. [14] used Aspen Plus, a commercial software package, to simulate the cement clinker production focusing on clinker chemistry and thermodynamics in the rotary kiln.

The scope of the study was defined to meet the requirements of testing and implementing selected alternative fuels. Aspen Plus software was initially selected to model the cement manufacturing process of a regional cement plant from which required data was collected. Due to some difficulties in acquiring and using this software package and the lack of
technical support, the use of the Aspen Plus model for this study was discontinued. Instead, a Microsoft Excel model is used to investigate suitable waste processing techniques to satisfy the storage, handling and feed requirements. Optimum blending ratios of alternative fuels with the fossil fuel are also studied by using the model. Among the selected alternative fuels, a comparative discussion is appended on the basis of the simulation results.

2. Alternative fuels

Fossil fuels are most commonly used in the cement industry due to their availability and price. In recent years, due to increasing prices and concerns over climate change, industry has been looking at alternative fuel sources which may be able to partially or totally replace fossil fuels. In the past couple of decades there has been a large amount of research on alternative fuels and their impact on plant performance. The cement plant has the additional advantages of high temperatures and long residence times within the kiln, and fuels normally considered dangerous to burn can be used in these circumstances. Almost all wastes have some calorific value which could be harnessed. However, in order to be economically viable they must meet a number of criteria, the most important of which are listed below [15]:

- Availability.
- Physical state of the fuel (solid, liquid, gaseous).
- Content of circulating elements (Na, K, Cl, S).
- Toxicity (organic compounds, heavy metals).
- Composition and content of ash.
- Content of volatiles.
- Calorific value (typically over 8 MJ/kg is required).
- Physical properties (scrap size, density, homogeneity).
- Grinding properties.
- Humidity content.

In order to create the model, the full chemical breakdowns of each of the fuels are required; this information was gathered from previous studies [6-7]. The current study allows the demonstration of the application of computer modelling to fuel analysis. Three potential alternative fuels, namely spent carbon linings, used industrial lubricants and used tyres have been selected for the current study because of their availability. Though the chemical breakdown of these selected fuels are available in the literature, to ensure the most realistic result, actual plant data have been collected from a regional cement plant. All three alternative fuels have been used or are currently being used by that cement plant. Chemical composition of the alternative fuels, feed material and the coal were collected from the referenced cement plant. Energy and feed material requirement of the process is determined on the basis of the collected data by using a computer model.

End-of-life tyres are a waste product from the automobile industry and became very popular to the cement manufacturers as an alternative fuel to cope with the increasing fuel costs during the mid 80’s. High carbon content, high heating value and low moisture content make discarded tyres one of the most used alternative fuels in the cement industry all over the world. Reinforcing wires of tyres can be consumed as a replacement for other raw material containing iron [16] when the whole tyre is used as alternative fuel.

Spent carbon lining (SCL) is a solid waste produced during the manufacture of aluminium metal in electrolytic cells. The carbon portion of the lining serves as the cathode for the electrolysis process. Up to 79% of U.S.-generated SCL was recycled in cement kilns in 2010 [17]. In 2009, 7449 tonnes of SCL were recycled in Australia, mostly in the cement industry as an alternative fuel [18]. Used industrial lubricants generally have high calorific value, and those can be used in cement kilns as alternative fuel with minimal processing cost [19]. The energy content of used lubricants varies due to the different ratios of various chemicals in it, although in most cases the calorific value of used lubricants is higher than coal.

3. Modeling and simulation

A range of simulation packages are available in order to model the complex chemical processes within modern cement manufacturing plants. Amongst them, ASPEN PLUS, ASPEN HYSYS and ANSYS FLUENT are widely used to model the manufacturing process and to predict the performance characteristics of the plant. ASPEN PLUS and ASPEN HYSYS use a flow sheet simulator to graphically represent each stage of the process allowing for, at a glance, interpretation of the stages of the process. ASPEN PLUS and ASPEN HYSYS enable quick and easy alterations to a process, allowing users to quickly trial a number of different system configurations without requiring a new model for each change. ANSYS FLUENT allows modeling of the effect of surface condition of the material as well as the effect of phase changes on a body of material. It also allows the optimization of fluid flow, material feed and containing structure. Due to the nature of cement production,
ASPEN PLUS is identified as the most suitable since this package has the ability to simulate chemical reactions within solid, liquid and vapour phases [20].

Modeling of the cement manufacturing process can also be done in Microsoft Excel. The Microsoft Excel model is much simpler than the other model; however, this model is not able to consider the chemical processes, the physical layout of the plant or the thermal properties of the materials. In this study, Microsoft Excel is used for modeling as there were some technical difficulties with the Aspen Plus software which we have a license for and due to the unavailability of technical support. The Microsoft Excel simulation is done based on the required input in order to account for the output. The outcomes of this model are sufficient to predict the overall effects of the alternative fuels on the feed requirements of the cement plant, but cannot account for any changes in the chemical composition due to the alternative fuels. Creating the Excel model can be broken into two distinct considerations: energy required by the process and the feed material required by the process. For the purposes of this model, the energy required was simplified to 3.05 mega joules per kilogram. The energy output and composition of each fuel set is shown in Table 1. The fuel required to generate the required energy is calculated using the following equation.

\[
Fuel_{Req} = \left( \frac{Energy\ required \times Clinker\ Produced}{Energy\ per\ kg\ of\ fuel\times Fuel\ %} \right)_{Fuel1} + \left( \frac{Energy\ required \times Clinker\ Produced}{Energy\ per\ kg\ of\ fuel\times Fuel\ %} \right)_{Fuel2} + \cdots (1)
\]

The primary purpose of this study was to identify the properties of the fuels being tested in terms of their effect on the cement manufacturing process. Additionally, this study identified the requirements for storing, handling and feeding of these fuels. While calculating the emissions for each fuel, only carbon dioxide has been considered. This was calculated under an ideal case where all carbon atoms are reacted to CO₂. This assumption is suitable for the purposes of this study and, when applied in the same way to all fuel options, provides a suitable comparison between the fuel outputs.

The generalized data from a number of sources and the actual plant data from the regional cement plant are used to run the model. The required information was split into the following categories:

**Fuel Properties:** The properties of the alternative fuel in terms of energy content and chemical composition were needed in order to calculate the amount of fuel needed and the various emissions.

| Table 1: Fuel Composition |
|---------------------------|
| **Energy Content (MJ/kg)** | Coal | SCL | Tyres | Used Oil |
|---------------------------|------|-----|-------|----------|
| Water                    | 8.1  | —   | —     | 1.0      |
| Carbon                   | 69.9 | 36.59| 72.0  | 74.2     |
| Hydrogen                 | 0.379| —   | 6.07  | 15.0     |
| Nitrogen                 | 0.15 | —   | 0.2   | 1.8      |
| Sulphur                  | 0.37 | —   | 1.06  | 1.34     |
| Oxygen                   | 6.32 | —   | 1.12  | —        |
| SiO₂                     | 8.2957| 10.2| 2.292 | 0.31     |
| Al₂O₃                    | 4.07 | 18.4| 3.056 | 1.4      |
| Fe₂O₃                    | 1.193| 3.0 | 12.5247| 4.95     |
| CaO                      | 0.3  | 1.9 | 0.4011| —        |
| MgO                      | 0.168| 0.81| 0.6112| —        |
| K₂O                      | 0.267| 0.7 | —     | —        |
| Na₂O                     | 0.0487| 14.0| 0.665 | —        |
| SO₂                      | 0.4386| —   | —     | —        |
| F                        | —    | 14.4| —     | —        |

**Material Feed:** To calculate the contribution of the fuel to the raw material required by the process, the material content of the fuel had to be known.
The proposed Microsoft Excel model could not simulate chemical reactions but could predict the suitability of fuels based on the required material input. The feed material content required and the content of the alternative fuels are taken from the available cement manufacturing plant data. The resulting feed material was calculated using the following equation.

\[ \text{FeedReq}_{\text{Material}} = (\text{Mass Fraction} \times \text{Output}) + (\text{Mass Fraction} \times \text{Output} \times \text{Loss on Ignition}) \]  

Due to the simple nature of the model, the following assumptions were made:
- There were no chemical reactions accounted for.
- The feed required only related to the total input required and did not account for feeding fuel into the preheater or kiln.
- The emissions were calculated as an ideal conversion of carbon to carbon dioxide; this was necessary to allow excel to calculate emissions.
- Energy requirement was assumed to be 3.05 mega joules per kilogram of clinker production.
- Assuming that 100kg of clinker was to be produced, the required feed material is shown in Table 2. According to the previous assumption, the total energy required is 305MJ.
- To meet the energy requirement, the required amount of coal was 11.12 kg which was calculated on the basis of the assumptions stated earlier.

Table 2: Feed Material Required

| Component | Mass % | Required (kg) | Loss on Ignition (kg) | Final Requirement (kg) |
|-----------|--------|---------------|-----------------------|------------------------|
| SiO₂      | 21.84% | 21.84         | 7.788                 | 29.628                 |
| Al₂O₃     | 5.72%  | 5.72          | 2.040                 | 7.760                  |
| Fe₂O₃     | 3.89%  | 3.89          | 1.387                 | 5.277                  |
| CaO       | 66.55% | 66.55         | 23.732                | 90.282                 |
| MgO       | 1.10%  | 1.10          | 0.392                 | 1.492                  |
| K₂O       | 0.37%  | 0.37          | 0.132                 | 0.502                  |
| Na₂O      | 0.31%  | 0.31          | 0.111                 | 0.421                  |
| SO₃       | 0.22%  | 0.22          | 0.078                 | 0.298                  |
| Total     | 100    | 100.000       | 35.660                | 135.660                |

With a working simulation model, the next step was to run the required simulations in order to produce a set of results suitable for analysis. Using the Excel spreadsheet, production of the results was a simple process of changing the percentage inputs for each fuel. The testing took place in two phases, the first to test each fuel against coal and the second using a combination of the alternatives in order to select the most beneficial mixture. For each fuel composition test, the following procedure was used:
- Set the fuel percentage for the composition to be tested.
- Make up to 100% using coal.
- Check the results to ensure no component is oversupplied.
- If material is over supplied, reduce the step size to best pinpoint the limiting point.
- Repeat the process of checking the amount of the components until either a limit point is found or 100% of alternative fuel is used in the mixture.

4. Results and discussion

Three different alternative fuels for the cement industry have been studied through use of a Microsoft Excel model. The input data consisted of an energy requirement, amount of feed material required and the chemical composition of the feed material and fuels. The model provided the percentage changes in different components of the required feed material as well as changes in CO₂ emission. Figure 2 shows the resultant component breakdown for the 100% exchange of coal with different alternative fuels. This result gives an idea of the possible maximum exchange rate of coal to the alternative fuels. The changes in feed material requirements have been plotted in Figure 3 for the usage of the maximum limit of each
alternative fuel. Figure 3 indicates that SCL reduces the feed material requirements more than the other alternative fuel options.

**Fig. 2. Comparative component breakdown for 100% exchange of coal to alternative fuels**

**Fig. 3. Change in feed material required for different alternative fuels**

4.1. Spent carbon lining

Upon examination of the results of replacing the coal with SCL it was found that SCL is a viable substitute. The use of SCL does not provide significant thermal energy; rather it reduces the feed material requirements and is a source of fluorine. The disadvantage of using SCL is an increase in carbon dioxide emissions. The limiting factor for the use of SCL is the sodium oxide or alkali content which in this case limits the feed rate to 7.8% of the total fuel feed.
In terms of energy content and emissions savings, SCL is the worst performing of the tested alternative fuels. Due to the low energy content of SCL, it required 2.42 times of the amount of coal and produced 79% more carbon dioxide. At the limiting point, SCL increased the CO\textsubscript{2} emissions by 6.18% resulting in an additional 1.76kg of CO\textsubscript{2} when assuming that all carbon is converted to CO\textsubscript{2}. SCL is a very good source of the feed materials required for the process, amounting to 14.83% of the total requirements at the limiting point.

4.2. Used industrial lubricant

It was found that the use of used industrial lubricants was beneficial to the process. This fuel was able to produce the required energy with two kilograms less fuel compared to coal. CO\textsubscript{2} emissions increased 13% while coal is completely substituted by used industrial lubricants. The largest concern is that many used lubricants can be treated for reuse which is a more sustainable option. As such, burning in cement kilns should be a last resort and undertaken only for material which is too contaminated for recycling.

This study was able to show that, for the specific used lubricant considered, the energy and emissions make it a suitable replacement for coal. However, before implementation, the specific material to be used should be analysed to ensure that it will reduce the required feed material and CO\textsubscript{2} emissions. Used industrial lubricants were found to be the simplest alternative to implement. Due to the liquid nature of the material, the storage and handling equipment requires little space and can be easily incorporated into an existing plant.

4.3. Used tires

Used tires were shown to require 1.2 kg less material than coal in order to generate the required energy. Used tires produced 9% less carbon dioxide than pure coal. In addition, tires are a good source of iron due to the steel strapping within the rubber. The incineration of used tires is a sustainable practice as the recycling applications currently cannot consume the amount of material generated. Combustion of tires in the kiln was found to be a clean process due to the very high temperature and long residence times. In this study the tires were assumed to combust instantaneously. If the whole tire is not combusted entirely, that can result in less efficient firing and additional fuel requirement. Further study should be undertaken on specific firing situations to quantify the effect of this.

Storage handling and feeding of tires can be problematic, particularly if the tires are being fed in whole. The feeding involves a high level of manual handling. This can be overcome through the use of shredded tires, but the shredding equipment involves a higher capital cost and energy for preparation.

5. Conclusions

This study investigated three alternative fuels which were selected and analyzed for their suitability for use in a cement kiln. This analysis identified the benefits or detriments to the process using a computer simulation of the required process inputs. With suitable data being available for each of the fuels, a Microsoft Excel model was used to create a simplified solution. While this model was not able to calculate the chemical output, it was able to find the changes to the material input caused by each fuel which, for this study, was enough to make a preliminary judgment on the fuel’s suitability.

In the case of the spent carbon lining, it was found to be a suitable alternative fuel. Uniquely, this alternative is recommended for use not because of its value as an energy source, but for its ability of offset a portion of the feed material required. SCL was limited though by its sodium content which could not exceed the maximum overall input for the feed requirements. This fuel was found to be the easiest to implement as the storage, handling and feed requirements are very similar to that for coal and would require minimal alterations.

Used industrial lubricants were found to be the fuel most suited to replacing coal. The energy content for the used lubricants analyzed was the highest of all the fuels examined and produced the lowest overall carbon dioxide emissions. In terms of the change in feed material, this fuel provided little to no material and therefore the cost of the additional feed would need to be weighed against the savings in coal. The logistics of using waste lubricants is fairly simple and would require minimal changes to the current plant. The largest modification would be the area needed for the storage, pumping and blending.

As an alternative fuel, used tires were found to be a suitable replacement for coal. The tires had a high energy content allowing them to provide a better emissions profile than coal. The largest weakness with using this option is that tires require a complicated handling setup which often includes a large amount of manual handling.

Overall this study has successfully identified the strengths and weaknesses of each of the fuels considered. This study has proven that this process could be used to model an alternative fuel without the need for expensive testing, allowing many
more fuels to be considered, and having substantial benefit to both plant operators and the sustainability of the cement industry.

References

[1] WHD Microanalysis Consultants, 2011. Cement History. http://www.understanding-cement.com/history.html [Accessed 10 October 2011]

[2] Hendriks, C.A., Worrall, E., de Jager, D., Blok, K., Riemer, P., 2004, Emission Reduction of Greenhouse Gases from the Cement Industry, IEA Greenhouse Gas R&D Programe. Breakeley, 2004. Lawrence Berkeley National Laboratory, http://www.wbcsdcement.org/pdf/itl/prghgt42.pdf, ed. [Accessed 10 October 2011]

[3] Hewlett, P.C., 2003, Lea's Chemistry of Cement and Concrete. 4th ed. United Kingdom: Butterworth-Heinemann ltd.

[4] European Commission, Reference Document on the Best Available Techniques in the Cement and Lime Manufacturing Industries. BAT Reference Document (BREF), European IPPC Bureau, Seville, Spain, 2011.

[5] Vdz Media release, 2009, Environmental Data of the German Cement Industry, www.vdz-online.de/uploads/media/Environmental_data_2009.pdf [Accessed 19 June 2012]

[6] Kaantee, U., Zevenhoven, R., Backman, R., Hupa, M., 2004, Cement Manufacturing Using Alternative Fuels and the Advantages of Process Modelling, Fuel Processing Technology, 85 (4), p. 293–301.

[7] Lechtenberg, D., 2009, Spent Cell Linings from The Aluminium Smelting Process as an Alternative Fuel and Raw Material for Cement Production, Global Cement Magazine, January, p. 36-37.

[8] Ranade, V.V., Mujumdar, K.S., 2003, CFD Simulations of Solid Motion in the Transverse Plane of Rotating Kilns, Third International Conference on CFD in the Minerals and Process Industries, CSIRO, Melbourne, Australia, 2003.

[9] Ranade, V.V., 2003, Modeling of Rotary Cement Kiln, Third International Conference on CFD in the Minerals and Process Industries, CSIRO, Melbourne, Australia, 2003.

[10] Mastorakos, E., Massias, A., Tsakiroglou, C.D., Goussis, D.A., Burganos, V.N., 1999, CFD Predictions for Cement Kiln Including Flame Modeling, Heat Transfer And Clinker Chemistry, Applied Mathematical Modelling 23, p. 55–76

[11] Mujumdar, K.S., Ranade, V.V., 2006, Simulation of Rotary Cement Kilns Using a One-Dimensional Model, Trans IChemE, Part A, Chemical Engineering Research and Design, 84(A3), p. 165–177

[12] Mujumdar, K.S., Ganesh, K.V., Kulkarni, S.B., Ranade, V.V., 2007, Rotary Cement Kiln Simulator (RoCKS): Integrated Modelling Of Pre-Heater, Clinker, Kiln And Clinker Cooler, Chemical Engineering Science. 62, p. 2590 – 2607

[13] Marin, O., Charon, O., Dugue, J., Dakhan, S., Zhou, W., 2001, Simulating the Impact of Oxygen Enrichment in a Cement Rotary Kiln Using Advanced Computational Methods, Combust. Sci. and Tech. 164, p. 193-207

[14] Zhang, Y., Cao, S., Shao, S., Chen, Y., Liu, S., Zhang, S., 2011, Aspen Plus-Based Simulation of a Cement Calciner and Optimization Analysis of Air Pollutants Emission, Clean Techn. Environ Policy, 13(3), p. 459–468

[15] Mokrzycki, E., Uliaz-Bochenzycz, A., 2003, Alternative Fuels For The Cement Industry, Applied Energy, 74, p. 95–100.

[16] Kaantee, U., Zevenhoven, R., Backman, R., Hupa, M., 2002, Cement Manufacturing Using Alternative Fuels and the Advantages of Process Modelling, in Proc. of R2002 Recovery Recycling Re-Integration, Geneva, February 12-15.

[17] Alcoa Worldwide Sustainability: Sustainability of Operations: Environmental: Emissions & Waste, 2012, http://www.alcoa.com/sustainability/en/info_page/operations_env_emissions.asp. [Accessed 1st March 2012]

[18] Alcoa in Australia: Environmental Management: Waste, 2012, http://www.alcoa.com/australia/en/info_page/environ_waste.asp. [Accessed 1st March 2012]

[19] de Vos, S., Gortzen Mulder, J.E., Ligthart, T., Hesseling, W., 2007, LCA of Thermal Treatment of Waste Streams in Cement Kilns in Belgium, TNO report I&T-A R 2007/036, Netherland Org. for Applied Sci. Res.

[20] Aspen One. 2011. Aspen Plus. Product Disclosure Statement. Houston, TX USA: AspenTech AspenTech.

[21] Ansys, 2011. Ansys Fluent Features. Product Disclosure Statement. Ansys.