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Engineering and Environmental Assessment Framework for Calcined Clays as a Supplementary  
Cementitious Material

by

Daniela Maria Martinez Lopez

A dissertation submitted in partial satisfaction of the  
requirements for the degree of

Doctor of Philosophy

in

Engineering – Civil and Environmental Engineering

in the

Graduate Division

of the

University of California, Berkeley

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Professor Paulo J. M. Monteiro, Chair

Professor Arpad Horvath, Co-Chair

Professor Claudia Ostertag

Professor Stefano Schiavon

Fall 2021

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## Abstract

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An average of 0.9 tonne of CO<sub>2</sub> is released for each tonne of clinker produced worldwide. Around 0.5 tonne of CO<sub>2</sub> originates from the decarbonation of limestone, and on aggregate are considered to be the largest non-combustion source of CO<sub>2</sub> emissions from industrial production. The remaining CO<sub>2</sub> releases are mainly due to the fuel combusted during manufacturing of clinker and in the corresponding supply chains. In light of the scale and urgency of climate change, development of environmentally less damaging cements as well as improvements in concrete production have been explored by many researchers. While upgrading current plants with new technologies is costly and has already been done in most countries, the use of supplementary cementitious materials (SCMs) has shown to be the most cost-effective approach to reducing emissions from cement manufacturing. However, slag and fly ash, the two most used SCMs of suitable quality for clinker replacement, are concentrated in regions where coal power plants and steel plants are located, and the transition to cleaner and more efficient technologies for energy generation and steel manufacturing are limiting their use as a long-term solution. For this reason, there is a vital need to find readily available alternative materials for widespread use as partial replacement of clinker.

In this dissertation, the use of metakaolin (calcined clay) coupled with limestone as SCMs for partial replacement of clinker in cement is explored. Both their mechanical performance in mortar and concrete mixtures and their effects in reducing cement's and concrete's environmental burden are the main foci of this thesis. The importance of calculating the environmental impact of concrete binder made of cement, limestone, and metakaolin would allow us to understand their performance in reference to conventional concrete made of portland cement and commercially available Pozzolan-Portland-Cement concretes. In order to evaluate their environmental performance, Life-Cycle Assessment (LCA) of cements containing metakaolin is developed, along with a Life-Cycle Inventory (LCI) of each of its components. To this extent, a detailed description of an Excel-based

tool, the MK-LCA Tool, is presented as a method to evaluate the cradle-to-gate environmental impacts of metakaolin by unit of mass. The environmental evaluation accounted not only for the direct emissions obtained from the production process, but also for indirect, supply-chain impacts of electricity generation and fuel pre-combustion. With an accurate evaluation of the emissions originating from manufacturing, the application of these materials in clinker replacement can be evaluated as a method to reduce cement's, and in turn, concrete's environmental footprint. Applications of the tool with a case study located in California showed a strong correlation between the global warming potential (GWP) of metakaolin's production and the fuel used for its calcination, with values ranging from 340 kg CO<sub>2</sub>-eq/tonne to 46 kg CO<sub>2</sub>-eq/tonne when petroleum coke and waste wood were used, respectively. When included as SCM in ternary cement blend comprising clinker and limestone with a total substitution of 50% (i.e., 35% metakaolin and 15% limestone), significant reductions of greenhouse gas (GHG) emissions and life-cycle energy demand were achieved compared to portland cement (36% lower emissions and 19% lower energy demand when metakaolin was calcined using a dry rotary kiln, and 39% lower GHG emissions and 24% lower energy demand when using a flash calciner). When compared to commercially available blended cements, the ternary blends with metakaolin and limestone showed the lowest GWP, and energy demand was surpassed only by slag cement since the latter comprises an average replacement ratio of 85% of clinker by slag. However, all of the blended cements containing fly ash showed higher GHG intensities compared to the ternary blend with metakaolin and limestone cement (i.e., 16-42% increased GHG emissions). Additionally, data on the effect of the metakaolin-to-limestone ratio of ternary mortar blends on the mechanical performance and resistance to chloride penetration are also presented. It was observed that compressive strength is improved with the increase of limestone even for lower grades of calcined clay (i.e., low calcined kaolinite content). Furthermore, the transport properties are much improved with respect to those from portland cement concretes, which translates to more durable cement binders, demonstrating the ample applicability of these ternary cement blends. The development of ternary blends studied in this dissertation made with portland cement, calcined clay, and limestone at industrial scale will have the potential to contribute to 30-50% global reduction of GHG emissions from the cement industries with a focus on emerging economies that would benefit from low-carbon cements without the technical and economic challenges that limit the implementation of other highly technical solutions such as carbon capture and storage.

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# Glossary

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**Binders:** Referred herein as materials that have cementitious properties (e.g., portland cement).

**C<sub>2</sub>S:** In cement chemistry notation indicates  $2\text{CaO}\cdot\text{SiO}_2$ .

**C<sub>3</sub>A:** In cement chemistry notation indicates  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ .

**C<sub>3</sub>S:** In cement chemistry notation indicates  $3\text{CaO}\cdot\text{SiO}_2$ .

**C<sub>4</sub>AF:** In cement chemistry notation indicates  $4\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot\text{SiO}_3$ .

**Clinker:** Principal ingredient of portland cement. Heterogeneous mixture produced by high-temperature reactions between calcium oxide and silica, alumina, and iron oxide [1].

**C-S-H:** Calcium silicate hydrates.  $\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$ .

**Environmental impact:** Consequence of environmental releases that could potentially cause an environmental problem if released in sufficient quantities and/or occur near flora or fauna (including human beings).

**Functional unit:** A clear and quantifiable measure that relates a function to the inputs and outputs of a product system [2].

**GGBFS:** Ground granulated blast furnace slag.

**GHG:** (Greenhouse gas) Corresponds to gases in the atmosphere (e.g., water vapor, carbon dioxide, methane) that absorb and emit radiant energy within the infrared range, thus producing the greenhouse effect in the Earth's surface.

**GWP:** (Global warming potential) Potential global warming impact of a gas. It is measured as the potential of a greenhouse gas to absorb energy over a period of time relative to the energy absorbed and released by the same amount of carbon dioxide gas.

**Interground:** Refers to clinker and other cementitious materials that are ground together in a mill.

**Life-cycle assessment (LCA):** Evaluation of inputs and outputs of a product or service throughout its entire life-cycle (e.g., cradle to grave) in order to estimate the environmental impacts of such product or service.

**Life-cycle inventory (LCI):** Collection of inputs and outputs (e.g., materials, emissions) that are used and emitted throughout the product's life-cycle within the system boundary defined in the study.

**Metakaolin:** Clay that contains kaolinitic mineral and has undergone thermal treatment. Also known herein as calcined clay.

**Overground:** Refers to clinker and/or other cementitious materials that are overly ground beyond their optimum fineness.

**SCMs:** (Supplementary cementitious materials) Also known as mineral admixtures, are finely divided siliceous materials that could have cementitious or pozzolanic characteristics or both. These materials are normally added as partial replacement of cement in mortar and concrete applications.

**System boundary:** Subset of the collection of processes and flows of the product system that is the focus of the life-cycle assessment.

**Underground:** Refers to clinker and/or other cementitious materials that are poorly ground or not ground to their optimum fineness.

**w/b:** Water to binder ratio. Relationship between the anhydrous cement particles and the water in the cement paste.

# Introduction

---

Portland cement concrete is the most widely used material in the world after water. Cement, the principal ingredient of concrete, when combined with water, produces hydration products capable of binding aggregates. However, cement's manufacturing is responsible for about 8% of total humans' carbon footprint. The biggest emissions occur during the pyroprocessing of the raw materials, specifically limestone which undergoes a process of decarbonation releasing close to 0.5 kg of CO<sub>2</sub> per kg of cement produced. Limestone and clays are rendered reactive when subjected to the high temperatures of calcination (close to 1450 °C), which requires burning large amounts of coal and other fossil fuels. Burning of these fuels result in another 0.4 kg of CO<sub>2</sub> emissions per kg of cement. Recent advancements on cement and concrete technology have demonstrated a reduction of cement's CO<sub>2</sub> emissions based on strategies that target the efficiency of the burning process, the use of renewable fuel sources, the use of alternative raw materials for the production of cement, and the partial replacement of cement with supplementary cementitious materials (SCMs). This study focuses on the use of metakaolin (MK) as a supplementary cementitious material in cement, and presents a life-cycle assessment tool (i.e., MKC-Tool) that evaluates the environmental impact of MK and allows for the establishment of comparison with other SCMs used for less environmentally damaging cement and concrete production. Aspects related to the quality of the metakaolin to be used, as well as the optimum ratios of replacement in cement blends made with portland cement clinker, metakaolin, and limestone are also studied. Mechanical performance and the resistance to chloride penetration of mortar cubes and concrete cylinders made with these blends are also detailed in this work. Results showed that cement blends with metakaolin and limestone can be done without compromising the mechanical performance of mortar and concrete and with similar compressive strength than those obtained from mixes made with 100% portland cement after 7 days. In addition, blends composed of 50% portland cement, 35% metakaolin, and 15% limestone resulted in 14-39% reduction in carbon emissions compared to other commercially available cement blends in California.

## Scope

This dissertation discusses the environmental impact of current cement and concrete manufacturing processes, as well as the most widely adopted practices to mitigate cement's CO<sub>2</sub> emissions. The discussion is followed by describing the development of a tool namely, MKC-Tool to evaluate the environmental impact of metakaolin when used as a SCM in cement-based materials and in concrete applications. This work also shows applications of the tool to compute the total global warming potential of cement with partial replacement of metakaolin by using the life-cycle assessment methodology. In addition, a comprehensive experimental program that studies the effects of partial replacement of cement with a combination of metakaolin and limestone and their performance against chloride ingress and compressive loading is also detailed herein. Finally, the study allows for the establishment of comparisons involving greenhouse gas footprint and durability of mortar and concrete mixes containing metakaolin and limestone.

## Organization

Chapter 1 describes the environmental impacts of the concrete and cement industries worldwide and the state of the art of the mitigation strategies proposed to reduce CO<sub>2</sub> emissions associated with cement and concrete production. This chapter also discusses the importance of using supplementary cementitious materials as a path to reduce the clinker-to-cement ratio with emphasis in metakaolin (i.e., calcined clays) and limestone as the most sustainable sources of SCMs to provide a significant reduction in emissions and improve the environmental issues faced by this industry in the short and medium term.

Chapter 2 introduces the use of metakaolin as a SCM in cement blends composed of clinker, metakaolin, and limestone. It provides a new interpretation of the state of the art found in available literature. For this work, over 100 publications related to the study of calcined clay in cement, its applications, mechanical performance, and interaction with other raw materials as well as its environmental impact compared to ordinary portland cement were carefully reviewed and analyzed. It also discusses the gaps of knowledge in the area of environmental assessment of metakaolin production and the overall carbon footprint of cement blends containing the SCM and introduces the work done in this dissertation to fulfil those gaps.

Chapter 3 presents a laboratory experimental program on 270 mortar cubes and 135 concrete cylinders containing varying ratios of portland cement clinker, metakaolin, and limestone. This set of experiments investigates the influence of variations in the clay-to-limestone ratio on the compressive strength and chloride penetration resistance of mortar cubes and concrete cylinders. It was observed that both the mechanical performance and the resistance to chloride penetration is improved when a ratio of 35% metakaolin and 15% limestone (i.e., total substitution of 50%) is used.

Chapter 4 provides a description of the MKC-LCA Tool designed to estimate the environmental performance of metakaolin production from cradle to gate based on real (local) parameters. With this tool, cement/concrete manufacturers, decision makers in the construction sector and researchers can obtain a real validation of the benefit of implementing metakaolin in their mix designs.

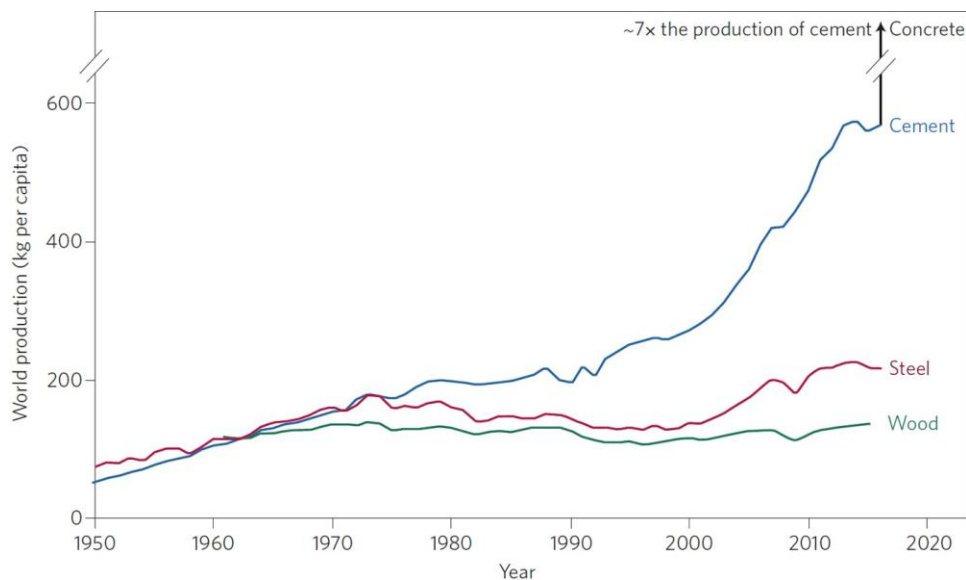
Chapter 5 investigates the environmental impacts of metakaolin production. the MKC-LCA Tool has been used to model the global warming potential (GWP) and energy demand of metakaolin for different scenarios of calcination technology and fuel mix input in California. In addition, this chapter also shows the GWP and energy demand of typical blended cements in California and identify the environmental benefits of cements made with clinker, metakaolin, and limestone compared to those made with fly ash and slag.

Chapter 6 discusses data quality issues related to the MKC-Tool including aspects of uncertainty and variability of data derived from the case studies discussed in Chapter 5. Different scenarios are also presented and evaluated against uncertainty parameters through a sensitivity analysis. A review on inventory data quality and data gaps is also detailed by means of a Pedigree Matrix.

Finally, Chapter 7 includes conclusion drawn from this research as well as recommendations for future related research.

# Chapter 1 – Concrete’s Environmental Impacts

The rapid industrial growth and urbanization for the past 70 years have significantly increased the consumption of concrete. Concrete production impacts the environment through the release of greenhouse gas (GHG) emissions into the atmosphere. The increasing demand for this construction material is related to concrete’s numerous attributes, such as low cost, ease of production, precise building code, excellent track record. Concrete’s constituents include a cementitious binder (e.g., portland cement), aggregates, water, and admixtures. Cement is the principal component in concrete, and binds aggregates forming a complex structural material. Current statistics estimate that the annual production of cement surpassed 4 billion tonnes in 2017, and it will continue to grow in the next decades [3]. Cement production increased more than ten times its corresponding value in 1950 in contrast to small growth (i.e., three-fold) in steel production and consistent production of wood, as shown in Figure 1.1.



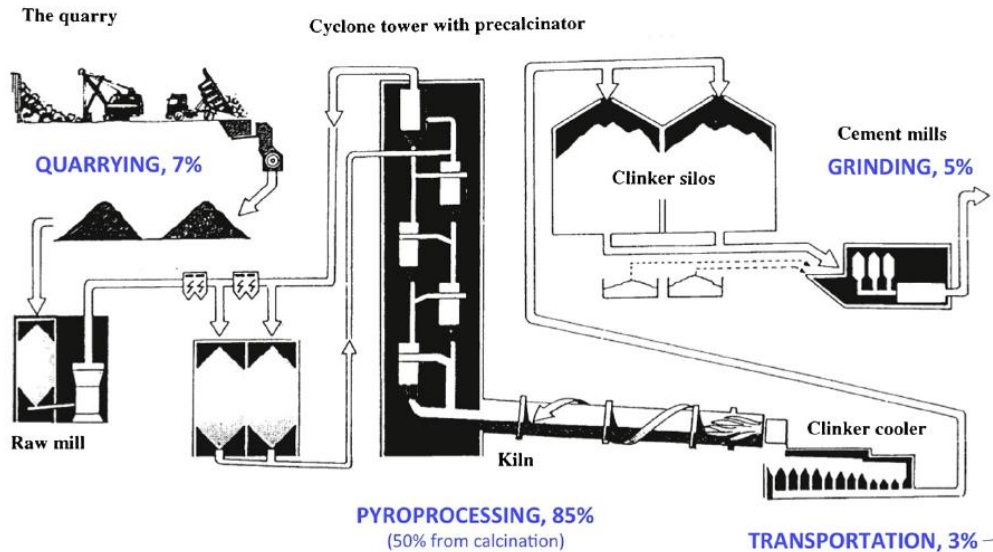
**Figure 1.1** – Historic world production (kg per capita) of the three most common construction materials (i.e., cement, steel, wood). Monteiro et al. developed this plot using historical data from the US Geological Survey and the Food and Agriculture Organization [4].

Concrete manufacturing is currently responsible for near 8.6% of global CO<sub>2</sub> emissions and 2.6% of total global energy demand [5]. Over 90% of these GHG emissions and 80% of the embodied energy are associated with the cement production. Two main components contribute to the environmental impacts of cement. The first one corresponds to the high global demand for this material, mostly from emerging countries. Researchers have proposed mitigation strategies such as the adoption of building design techniques based on climate-building interaction and the optimization in design and proportioning of concrete, taking into account environmental impacts, geometric aspects, and structural requirements [6, 7]. While recognizing that a decrease in the rate of cement consumption can play a significant role in reducing carbon dioxide emissions, this strategy is left out of the scope of the present work.

The second component corresponds to the emissions associated with cement manufacturing. Conventional portland cement (PC) is composed of clinker and gypsum, often in a 95:5 ratio. Clinker is the marble-sized product obtained from the thermal treatment of cement's raw materials (i.e., limestone and clay) in the kiln. This clinker is then ground and combined with gypsum to form cement. A large percentage of cement's carbon dioxide emissions comes directly from the production of clinker. Gartner [8] separated CO<sub>2</sub> emissions from this process into "Raw-materials CO<sub>2</sub> emissions" and "Fuel-based CO<sub>2</sub> emissions". The former occurs during the combustion process of calcium carbonate present in limestone as given by the following equation (1.1):



A significant amount of energy needs to be supplied to the kiln to bring the clinker to its optimal temperature of 1450°C. Thus, depending on the type of fuel used and the technology of the kiln in a plant, the "Fuel-based CO<sub>2</sub> emissions" may also be a large contributor to greenhouse gas emissions (Figure 1.2).



**Figure 1.2** - Distribution of CO<sub>2</sub> emissions from portland cement production process. After [9]

Habert et al. [10] calculated the total amount of annual emissions from concrete production using equation (1.2) below. Total emissions include those from raw materials processing (i.e., RM emissions) and those from the energy demand for cement production (i.e., Fuel emissions and Energy kiln).

$$tCO_2/yr = [(Fuel_{emissions} * Energy_{Kiln} + RM_{emissions}) * Clinker_{content}] * Production_{Cement}/yr \quad (1.2)$$

Where, Fuel<sub>emissions</sub> [tCO<sub>2</sub>/Mj]

Energy<sub>Kiln</sub> [Mj/tClinker]

$RM_{\text{emissions}} [\text{tCO}_2/\text{tclinker}]$

$\text{Clinker}_{\text{content}} [\text{tclinker}/\text{tconcrete}]$

$\text{Production}_{\text{cement}} [\text{t}_{\text{cement}}/\text{yr}]$

To reduce climate change impacts caused by the industrial sector in recent decades, researchers have focused on reducing the environmental impact of concrete production throughout the entire construction value chain. The following sections discuss several mitigation strategies that aim to reduce this burden and mostly target those emissions associated with cement manufacturing. Measures such as the improvement of kiln energy efficiency, the use of cleaner combusting fuels, the use of alternative energy sources, the use of alternative binders, the adoption of carbon capture during cement production, and the use of supplementary cementitious materials (SCMs) are discussed herein.

## 1.1 Mitigation Strategies to Reduce CO<sub>2</sub> Emissions

Researchers have proposed several strategies to minimize the environmental impact of cement production worldwide. As previously stated, cement's and concrete's global consumption would most likely continue to increase in the next century due to the high demand for new construction in developing countries [11]. For this reason, the improvement in cement's technology is the principal route to reducing concrete's carbon footprint. The following sections explain the main mitigation strategies most widely used nowadays: improvement in kiln energy efficiency, the use of cleaner-combusting fuels, the use of alternative energy sources for electricity, the use of alternative binders, and the use of SCMs. Carbon sequestration has been proven successful, but this field is still undergoing research, and wide-scale application is still under study [12]. However, I discuss it briefly in this chapter.

### 1.1.1 Increased Kiln Energy Efficiency

Clinker production starts with the decomposition of the raw material with high-calcium content (e.g., limestone). This stage is called calcination and comprises the formation of calcium oxide and the release of carbon dioxide at around 900°C. At higher temperatures (1450°C), the calcium oxide reacts with oxides of silica, iron, and alumina to form clinker phases. Clinker and gypsum are then ground together to form portland cement.

Raw materials for clinker need to be well mixed before heat treatment and depending on the source, they can be found wet or dry in their natural conditions. Their preparation generally includes crushing, grinding, and blending. In wet-process kilns, water is added for preparation, forming a slurry. This slurry requires extra energy to evaporate the water before it is fed to the kiln. For dry-process kilns, no water is added to the dry raw materials before the clinkering process. Dry and wet kiln systems in operation nowadays have energy efficiencies varying from 3000 to 6300  $\text{Mj}/\text{t}_{\text{clinker}}$ , respectively [13]. This variation is related to both the technology of the kiln and regional factors such as the natural state of the raw meal which could involve a dry, semi-dry, semi-wet or wet process. Gartner [8] estimated the total theoretical heat requirement for clinker formation at 1800  $\text{Mj}/\text{t}_{\text{clinker}}$  in a perfect system with no heat losses. However, this value is unlikely to be reached in industrial-sized kilns given the intrinsic heat losses from the materials available to insulate the kiln shells and the use of air for combustion of fuels. The use of pure oxygen proposes



an alternative solution to getting closer to the enthalpy requirement for clinker formation. However, the dangerous —and even more energy-intensive— approach of using pure oxygen instead of air for combustion of fuels, renders this solution impractical at industrial scale. Most of the kilns in the USA and Europe are already optimized to about 80% of their thermodynamic limit, placing them in the lowest end of the energy consumption range. Currently, the most energy efficient structure is the rotary kiln with multistage cyclone preheaters, precalciner, and heat recovery system. These kilns have an average energy consumption of 3200 Mj/t<sub>clinker</sub> when additional heat waste co-processing is not used, and 3000 MJ/t<sub>clinker</sub> for those who incorporate it.

Given the close reliance on fossil-based fuels to provide the kiln with the energy necessary to produce clinker, the “Fuel-based CO<sub>2</sub> emissions” from the different types of kiln varies widely (i.e., 0.31 kg CO<sub>2</sub>/kg<sub>clinker</sub> for a kiln with a specific heat consumption of 3100 Mj/t<sub>clinker</sub> to 0.6 kg CO<sub>2</sub>/kg<sub>clinker</sub> for a kiln with a specific heat consumption of 6000 Mj/t<sub>clinker</sub>) [14]. Higher thermal efficiency implies lower fuel consumption, hence, a reduction in GHG emissions from the “Fuel-derived CO<sub>2</sub> emissions” category. In addition, lower fuel consumption also results in a reduction in the costs associated with the acquisition of fuels to feed the kilns. Since bigger changes in a plant’s infrastructure can reduce the costs associated to energy consumption, the vast majority of modern cement plants worldwide are currently working with the best available technology, thus, new research on kiln optimization is unlikely to offer significant advances in energy efficiency for cement manufacturing in the near future. However, working with the best available technology implies significantly high investment costs for replacement or retrofitting of existing cement plants.

Reducing fuel consumption and improving the thermal efficiency of cement kilns face a sizeable initial barrier due to great investment costs, either to construct new kilns or retrofit existing ones. Consequentially, this approach is becoming less and less popular in many places around the world. For instance, trends from Europe’s cement industry show that investments for kiln retrofits are no longer encouraged in the continent [10]. In addition, cement demand would likely decline in developed countries and would most likely increase in emerging countries in the next decades [15]. This is highly concerning given that in developing regions where new urbanization and construction are exploding, kilns with high thermal efficiency are scarce due to the large investment costs associated with the replacement or transformation of older models that are still in function.

### **1.1.2 Use of cleaner-combusting Kiln Fuels**

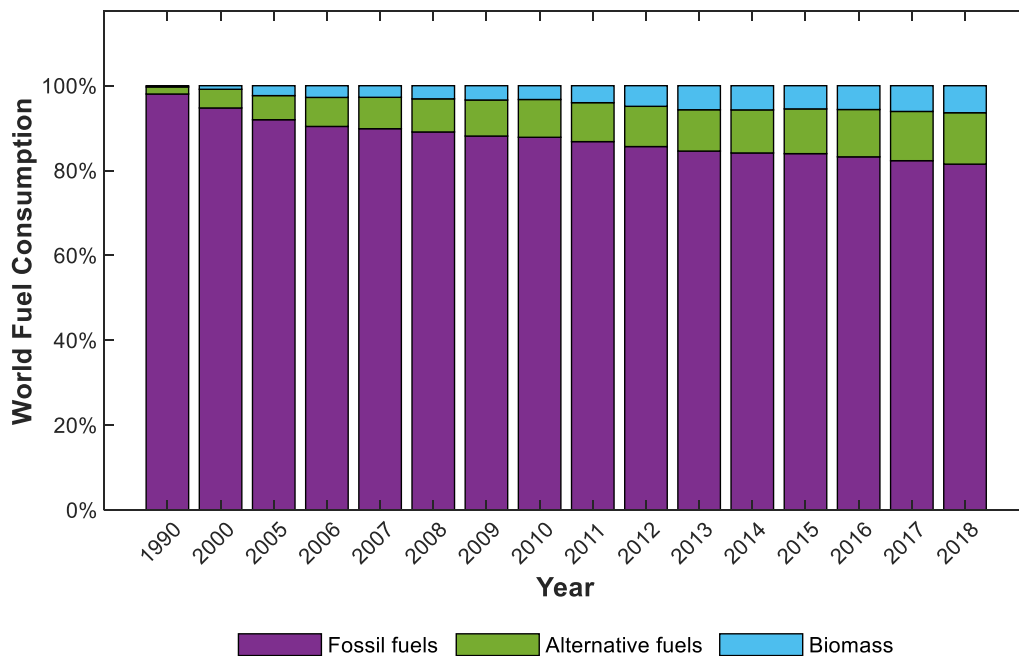
Fossil-based fuels have been traditionally used as combusting fuels for clinker production in kilns. These fuels provide relatively high heating values per mass basis to satisfy the high energy demand needed within the kiln during calcination of raw materials and clinker formation. Conventional fuels comprise coal, pet coke, natural gas, lignite, heavy oil, diesel oil, and shale oil. Upon combustion, these fuels release GHG emissions to the atmosphere contributing to the accelerating climate change. Since these fuels are mainly used for calcination of the raw materials in the kiln, a combination of increased energy efficiency in cement kilns and the increased use of alternative low/non-carbon-based fuels is important in the reduction of the overall carbon footprint of clinker production.

From alternative fuels, we should distinguish those that are considered carbon neutral. Carbon neutral fuels are those that have no net GHG emissions. Often, these fuels can offset the CO<sub>2</sub> emissions produced during combustion with a CO<sub>2</sub> intake during photosynthesis —producing

a system in equilibrium, hence the name carbon neutral fuels. These biomass fuels comprise forestry and agricultural biomass, biodegradable municipal waste, animal waste, and paper waste [14].

Another set of waste material suitable for combustion in the kiln are those derived from fossil fuel (e.g., solvents, plastics, used tires). These wastes have increased popularity in cement manufacturing given that the CO<sub>2</sub> reductions are significant when heat recovery occurs in the cement kiln. Heat recovery systems are not in place in regular incineration plants where these materials would naturally go. In addition, the toxic residues generated when burning fossil-based waste fuels for calcination are typically embedded into the resultant clinker, making it a feasible solution to otherwise a problem for the incineration plant [14].

The cement industry worldwide is moving towards the implementation of a dominant percentage of alternative fuels to further lower the environmental burden of cement. The use of these byproducts reduces the amount of waste that is taken to landfills and incineration plants. In addition, the reduction in the dependence of fossil-based fuels also translates into a reduction in costs from fuel acquisition. As shown in Figure 1.3, the use of alternative fuels and biomass is nowadays eight times more than that of 1990 [16]. Table 1.1 shows the net CO<sub>2</sub> emissions of the most common fuels used in Europe for kiln clinkerization process.



**Figure 1.3** – World kiln fuel consumption for the years 1990, 2000, and 2005-2018. Image developed using historical data from the Getting the Numbers Right (GNR) Project from the Global Cement and Concrete Association (GCCA) [16]

**Table 1.1** – Net CO<sub>2</sub> emissions from fuel combustion per energy output. Adapted from [10]

| <b>Fuel</b> | <b>CO<sub>2</sub> emissions per energy unit<br/>(g of CO<sub>2</sub>/Mj)</b> |
|-------------|--|
| Petcoke     | 101  |
| Coal        | 96   |
| Natural gas | 55   |
| Waste tires | 85   |
| Waste oil   | 74   |
| Plastic     | 75   |
| Waste fuels | 9  |
| Animal meal | 0  |
| Waste wood  | 0  |

### **1.1.3 Use of Alternative Energy Sources**

Similar to the use of cleaner fuels for calcination, the use of non-fossil energy sources contributes to a reduction in the overall environmental burden of cement production. This mitigation strategy is playing a big role in countries that are shifting their sources of energy for electricity generation to renewables such as wind, solar, and biomass, and for those countries that use non-carbon-based fuels for electricity generation such as nuclear power plants.

Although any contribution in the reduction of the overall environmental burden of cement production matters, the percentage of CO<sub>2</sub> emissions associated to electricity consumption of cement production and the regular operation of a cement plant, only makes up to 5% of the total carbon emissions from the entire cement production cycle [17]. The average consumption of electric power in a cement plant is approximately 0.4 GJ per tonne of clinker (106 kWh/t). However, this value could increase to up to 1.2 GJ per tonne of clinker if we consider the inefficiencies of electricity production and distribution [8]. From this electricity demand, the biggest percentage is utilized during the grinding process of the clinker and other supplementary materials in blended cements. The traditional grinding equipment used in most cement plant's is the ball mill. Newer and more efficient technologies include grinding by vertical rolls mills and by high-pressure grinding rolls. However, transition to the latter devices comprises high investment costs for either the procurement of a completely new grinder or the retrofitting of an existing one (i.e., 30 million euros for a new grinder and 6 million euros for retrofit) [18].

### **1.1.4 Use of Alternative Binders**

In this section I adopt the definition given by Miller and Myers [19] of alternative cement binders as those binders that can fully or partially replace conventional ordinary portland cement but do not fall into PC specifications. I separate these alternative binders into clinkered alternative cements (i.e., those in which a pyroprocessing stage is part of the cement's life-cycle) and alkali-activated materials.

### 1.1.4.1 Clinkered Alternative Cements

- Belitic Cements

These cements are rich in belite ( $\text{Ca}_2\text{SiO}_4$ ) which is the main reactive phase with alite ( $\text{Ca}_3\text{SiO}_5$ ) as the secondary reactive phase that is only produced in minor quantities. The process of production is similar to that of portland cement and it requires the same raw materials (i.e., limestone and silica). However, belite rich cements form at lower temperatures ( $1200^\circ\text{C}$ ) and they require less limestone per unit of belite phase produced. In addition, it releases less chemical  $\text{CO}_2$  (i.e., less RM emissions). The stoichiometric formula for the formation of belite is as follows:



The lower temperature of calcination and the release of less chemical  $\text{CO}_2$  reduces the overall emissions from production by 10% approximately [18]. In addition, these cements can be made with the same technology as portland cement in current cement plants so the additional investment costs are negligible. The main drawbacks from these cements are the significant lower reactivity of the belite phase compared to PC which is rich in alite phase, and the relatively low  $\text{CO}_2$  reduction potential given that their production still relies on limestone as the principal raw material which in all decreases their market penetration. Technologies that improve the reactivity of belite-rich cements are presented below. In some instances, belite is combined with phases of calcium-sulfo-aluminates ( $\text{C}_4\text{A}_3\text{S}$  or  $4\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot \text{SO}_3$ , mainly ye'elimite) and ferrite in different proportions to form either belite ye'elimite ferrite cements with some production in Europe or calcium (sulfo) aluminate cements with has a large market in China.

Reactive belite-rich clinkers (RBPC) surmount belite-rich clinkers explained above by the physical or chemical activation of their belite phase. The activation can be done by rapid cooling of the clinker and/or by adding low amounts (e.g., 0.5-1.0%) of  $\text{SO}_3$  in the meal [20]. Even though, these clinkers comprise the same portland cement clinker phases (i.e.,  $\text{C}_2\text{S}$ ,  $\text{C}_3\text{S}$ ,  $\text{C}_3\text{A}$ , and  $\text{C}_4\text{AF}$ —in cement's notation<sup>1</sup>), the main difference with PC clinker is their alite/belite ratio. One of the biggest drawbacks that persist on this reactive belite-rich cement as alternative binder is that it requires extra energy for the fine grinding of the resulting clinker which can offset a big fraction of the potential energy savings from calcination.

- Calcium (Sulfo) Aluminate-based Cements (CSA)

Originally developed by Alexander Klein in the 1960s as Type K expansive cement, these cements were used in the US for prestressed concrete construction. Type K cements contained great amounts of calcium sulforaluminate and calcium sulfate and were combined with PC to better control their expansive properties [1]. China has commercially produced cements that are rich in ye'elimite phase for over 40 years. These cements require a lower temperature in the kiln ( $1250^\circ\text{C}$

---

<sup>1</sup>  $\text{C}_2\text{S}$  corresponds to  $2\text{CaO}\cdot\text{SiO}_2$   
 $\text{C}_3\text{S}$  corresponds to  $3\text{CaO}\cdot\text{SiO}_2$   
 $\text{C}_3\text{A}$  corresponds to  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$   
 $\text{C}_4\text{AF}$  corresponds to  $4\text{CaO}\cdot 3\text{Al}_2\text{O}_3\cdot \text{SiO}_3$

to 1350°C) and lower amounts of limestone which reduces both the amounts of raw-materials and fuel-based CO<sub>2</sub> emissions. However, the main reduction in CO<sub>2</sub> emissions comes from the difference in their chemical composition in contrast to portland cement. The manufacturing process of traditional CSA cements uses the same technology as PC, but no silicate phases are present in these cements as their raw materials are mainly calcium carbonate (limestone), alumina (bauxite), and anhydrate (gypsum). The content of ye'elimite phase in these clinkers is typically between 60 and 70% of the total phases [8], thus, CSA cements rely heavily on aluminum-rich primary sources such as bauxites, clays, coal combustion ashes or municipal waste ashes for the production of this phase. However, the most common material used is bauxite which highly increases the overall price of these cements. Currently, these cements are only used in very specialized applications such as in the precast sector where the very rapid strength development and self-stressing abilities are important.

To widen the applications of sulfoaluminate-based cements, China developed an extension of these cements called the “Third Cement Series” which included ye'elimite as the major phase and belite and ferrite as secondary phases in lower quantities. However, these cements still face higher raw materials cost compared to PC due the use of bauxite to produce ye'elimite which is predominately the major phase. Depending on the ratios of ye'elimite, belite, and ferrite, these cements can emit 10-48% less raw-materials CO<sub>2</sub> emissions than conventional PC clinker [19].

#### ○ Belite-Ye'elimite-Ferrite Cement (BYF)

BYF cements were developed in Europe as a more affordable alternative to the Chinese CSA cements. BYF cements have three essential phases (belite, ye'elimite, and ferrite). Gartner and Sui [20] considered BYF clinker as an extension of the CSA cements with the intension of having a clinker that is more economical than CSA cements and could compete in the market with PC. In contrast to CSA cements, BYF clinkers contain lower amounts of the ye'elimite phase and significantly higher and more reactive amounts of belite and ferrite phases. This change in the ratios of the main phases allows for a more conventional manufacturing process (i.e., using the same rotary kiln for production) and a reduction of demand for the more expensive aluminum-rich raw material to produce ye'elimite phase. BYF cements produce less raw-material CO<sub>2</sub> because they require 20 to 30% less limestone to produce the belite phase in contrast with the chemical CO<sub>2</sub> emitted from the alite production in PC. This usually translates into 20 to 27% less chemical CO<sub>2</sub> emissions [19].

There are also some additional energy savings thanks to the lower kilning temperature which translates into less fuel demand and less fuel-based CO<sub>2</sub> emissions. However, these cements continue to work well only for very special applications such as precast concrete due to their variable setting and hardening times. Favier et al., in their report “Technology assessment for full decarbonization of the European industry by 2050” [18] considers that due to the high cost and very localized availability of bauxite (the main source of aluminum-rich raw materials), in addition to their limited application, BYF cements could substitute PC only by up to 10% by 2050.

- Carbonatable Calcium Silicate Cements (CCSC)

The main difference from PC clinkers is that CCSC react with  $\text{CO}_2$  instead of water to form solid products. The hardening mechanism of CCSC is not new. Rather, calcium silicates (main phases in CCSC) can harden by carbonation and by hydration as done by olden lime-based cements that mostly hardened by  $\text{CO}_2$  present in the atmosphere [20]. However, the main technological innovation with CCSC is the control of the carbonation process itself. This process can be effectively done by adapting the same technology for precast concrete curing to allow for the curing chambers to circulate the  $\text{CO}_2$ . However, additional investment costs are associated with the adoption of this process. These clinkers contain lower amounts of calcium relative to PC. The main raw materials utilized are forms of calcium silicates such as wollastonite and the absorption of carbon dioxide during the curing process can offset the amount of chemical  $\text{CO}_2$  from the decarbonation of limestone which leads to a potential  $\text{CO}_2$  savings of about 60% compared to PC [18]. In addition, these cements offer remarkable strength gains over 24 hours. The main drawbacks of CCSC are that they are mostly suited for precast elements that are thin enough to avoid differential hardening in the concrete and their lower pH compared to PC concretes limits their application with steel in reinforced concrete due to corrosion potential.

- Magnesium Cements

The main reactive phase of these cements is magnesium oxide (commonly known as periclase, MgO). Like CCSC, magnesium cements harden with carbonation instead of hydration. The most abundant source to produce magnesium oxide is magnesite rock ( $\text{MgCO}_3$ ). However, this process requires the calcination of  $\text{MgCO}_3$  in which it releases more chemical  $\text{CO}_2$  than limestone during the production of PC clinker. In other words, the environmental impact of producing clinker from  $\text{MgCO}_3$  (raw-material  $\text{CO}_2$  emissions) results in over 50% of total emissions from production. This leads to no reasonable justification to produce magnesium cements from  $\text{MgCO}_3$ . Another possible solution to produce a low-carbon magnesium cement is to derive magnesium oxide from the less common magnesium silicates.

Magnesium silicates are less abundant and located deeper in the earth's crust. Great levels of energy are needed for mining, and transportation costs are sometimes higher than those of raw materials for PC clinker. Furthermore, scalability of the production process from magnesium silicates hasn't been proven yet, and small scale trials face multiple challenges since they require several more steps and high pressure [18]. In addition, durability and mechanical performance, interaction with chemical admixtures, behavior under a wide range of temperatures, and early strength development are yet unknown and requires further research [20]. Another path to produce magnesium oxide is by synthesizing this material from the desalination of seawater which produces MgO with higher purity than that obtained from dry calcination of natural rocks [21]. The process of synthesizing MgO from seawater requires the pre-treatment of the brine with an acid to lower the pH followed by the addition of a strong base to raise the pH and precipitate the magnesium [22]. In practice, this process often involves the use of lime which itself has to undergo a calcination process and the magnesium hydroxide that is produced has to further undergo calcination to form the final MgO. Although potentially less  $\text{CO}_2$  is released by the synthesis of MgO from desalination, the cement produced still faces the same challenges of scalability and performance as those described when using the parental rocks.

#### 1.1.4.2 Alkali Activated Cements (AAC)

These binders are also known as geopolymers and differ from portland cement in that the raw materials do not include limestone and they do not undergo a pyroprocessing stage. Rather, the raw materials —mainly a solid precursor and an alkali activator— are combined to form a binder that can set and harden. Traditional precursors for this type of binder are by-products of other industries that are rich in alumina or alumino-silicate minerals such as slags and high calcium fly ash. These alternative binders are considered low carbon emitters (40 to 80% lower emissions than PC [18]) given that they heavily rely on slags and fly ash. These materials are well known as waste products from the steel industry and the coal-fired power plants which also contributes to a reduction in the cost of production. However, the production of the alkali activator —typically sodium or potassium hydroxide and silicate [23]— is energy intensive and the CO<sub>2</sub> emissions from this activity are normally not considered in their overall environmental impact. Some of the drawbacks of these binders include the great variability in setting times and the conflicting interaction with chemical admixtures to improve workability. Currently, the main use of AAC is in the fabrication of precast elements. Furthermore, most of these binders that are capable of hardening in ambient temperature require the use of slag as a precursor. The limited and concentrated availability of this by product in the world and the competition for the production of blended cements that rely on slag as a supplementary cementitious material are the main reason why the alkali activated binders alone will not contribute to the significantly reduction of cement's CO<sub>2</sub> emissions. Nevertheless, in his white paper for the UNEP series on Eco-Efficient Cements, Provis [24] confirmed that even though AAC were not a one-to-one replacement of portland cement in every region and for every application, these binder could play an important role in the mitigation of cement's CO<sub>2</sub> emissions for those regions where raw materials were readily available and the footprint of the alkali activator was low enough to be considered feasible. Provis pointed out that a single value for the environmental impact of AAC could not be estimated and moreover could not be compared with that from portland cement without accounting for the regional context, origin of raw materials, energy mix used for their production, transportation of materials, among other factors as previously discussed by Habert and Oullet-Plamondon [23]. Moreover, the environmental impact of the alkali activator, which has been considered to be the principal contributor of these cements' CO<sub>2</sub> emissions was grossly overestimated based on a single study dating 1990 and had been adopted in LCA databases at present. More efficient methods for the production of alkali activators have been addressed since 1990 and thus should be studied more carefully to give a real estimation of the potential savings of AAC.

Other alternative binders with potentially reduced CO<sub>2</sub> emissions have been explored but these cements have not taken off in the market due to very localized raw materials or uncertainties in hardening and setting times. These cements are energetically modified cements, supersulfated slag cements, and hydrothermal reactive belite cements. I do not emphasize on the details of these alternative binders given that they do not provide considerable benefits in CO<sub>2</sub> reduction compared to portland cement or they require a change in the traditional production of clinker and their raw materials are considered scarce and very localized in few geographical locations. They are also not scalable to industrial scenarios of widespread applications. For example, these alternative binders are not considered as potential solutions in the European cement industry by 2050 [25].

### **1.1.5 Use of Carbon Sequestration Techniques**

The ability to capture carbon dioxide from emission-intensive processes allows to further reduce and sometimes completely offset the carbon emissions released from the process itself. The cement industry is looking into the adoption of techniques that could allow the capture of CO<sub>2</sub> and its potential use and storage. Limestone is the principal source of calcium that is readily available and in large quantities in the world. As we discussed before, the process of producing clinker from limestone releases great amount of CO<sub>2</sub> emissions into the atmosphere. Given the lack of abundance of a total replacement of limestone with a material equally capable of providing the same chemistry for clinker formation, the need to capture the CO<sub>2</sub> emitted calls for technologies of carbon capture and storage that require both large capital and operational investments.

In this work I distinguish between carbon capture and storage (CCS) as the carbon dioxide that is captured and stored underground permanently and carbon capture and use (CCU) as the CO<sub>2</sub> that is captured and used to produce other materials. The International Energy Agency (IEA) and the Cement Sustainability Initiative (CSI) from the World Business Council for Sustainable Development (WBCSD) released a Technology Roadmap report in 2018 with mitigation practices for the low carbon transition of the cement industry in order to achieve the global reduction targets of CO<sub>2</sub> by 2050 to limit the average global temperature rise to 2°C or lower by the end of the century. Such report highlights the importance of carbon capture techniques in the cement industry to meet the global reduction targets. However, current technical issues for scale applications and high capital investment costs render this mitigation strategy too difficult to implement in the short term [11].

Favier et.al [18] describes several technologies for carbon capture and storage that are currently under development or being slowly implemented in few cement plants located in North America and Europe. Estimated CO<sub>2</sub> reduction potential can be between 50 and 800 kg CO<sub>2</sub> per tonne of clinker. Regardless of the technology, the authors argue that the implementation of these technologies requires very high costs of investment (i.e., \$300 million Euros or two times the cost of a new cement plant) and a great increase in the electricity consumption (i.e., 2 to 3 times the current energy demand for electricity), which could offset the CO<sub>2</sub> reduction if the energy sources for electricity generation rely heavily on carbon-based fuels.

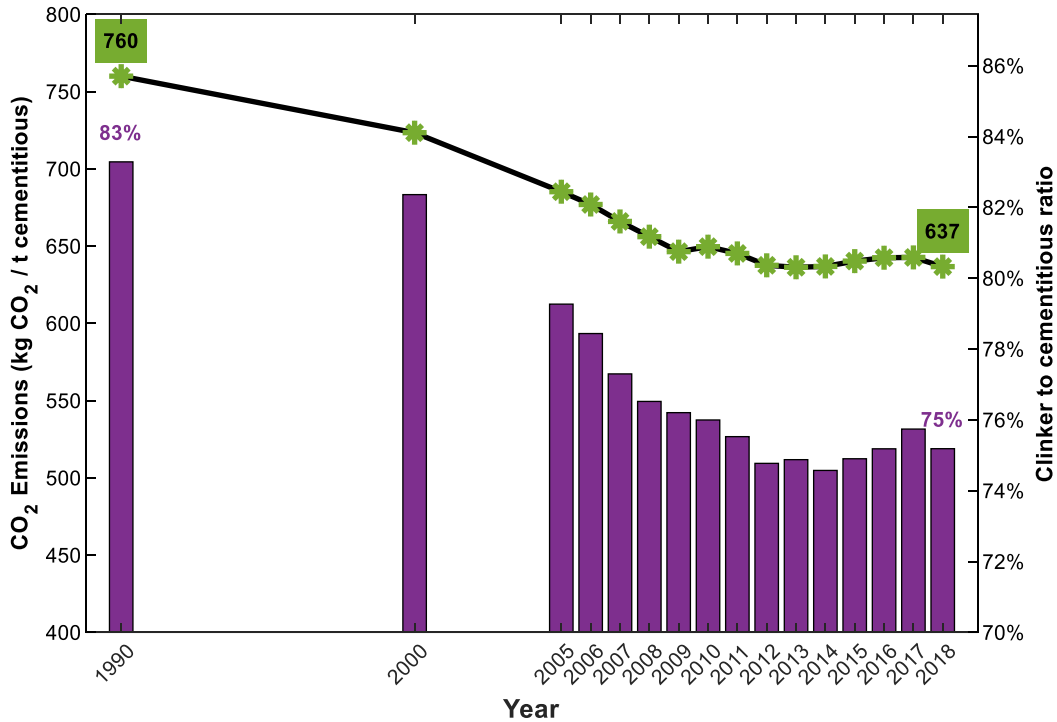
Technologies for carbon capture and storage should be implemented as a strategy to help achieve carbon neutrality of the cement industry. However, in order to have access to this technology that is still under study and implies large investment costs, the work of other readily implemented strategies should be massively adopted in combination.

### **1.1.6 Use of Supplementary Cementitious Materials in Blended Cements or in Concrete**

Clinker substitution and optimization should play the main role as a strategy to minimize the amount of CO<sub>2</sub> that must be captured from the clinker production. In order to meet this challenge sustainably, the solutions to the vast CO<sub>2</sub> emissions from cement need to be both practical and economically viable. As shown in Figure 1.4, SCMs can be used to offset CO<sub>2</sub> releases into the atmosphere from clinker production through two ways, depending whether substitution of clinker is performed at the cement production level after clinker formation or at the concrete production stage. Both practices are limited to a maximum standard percentage of replacement in order to avoid drops in strength, workability of the mix, and durability of the concrete. Pozzolans (a subset of SCMs) consist of reactive aluminosilicates that react with the calcium hydroxide from cement



hydration to produce more cementitious materials (e.g., calcium (alumino)silicate hydrates). A reduction in CO<sub>2</sub> emissions comes from the reduction of clinker content in the final cement product. In addition, a reduction in energy is also achieved since these SCMs require significantly lower or none calcination processing to achieve reactivity of the material. Among the most common SCMs are ground granulated blast furnace slag (GGBFS), fly ash, silica fume, natural pozzolans, rice husk ash, and calcined clays. Addition of pure limestone is also commonly used in ternary and quaternary blends of portland cement with other SCMs and will be also discussed herein.



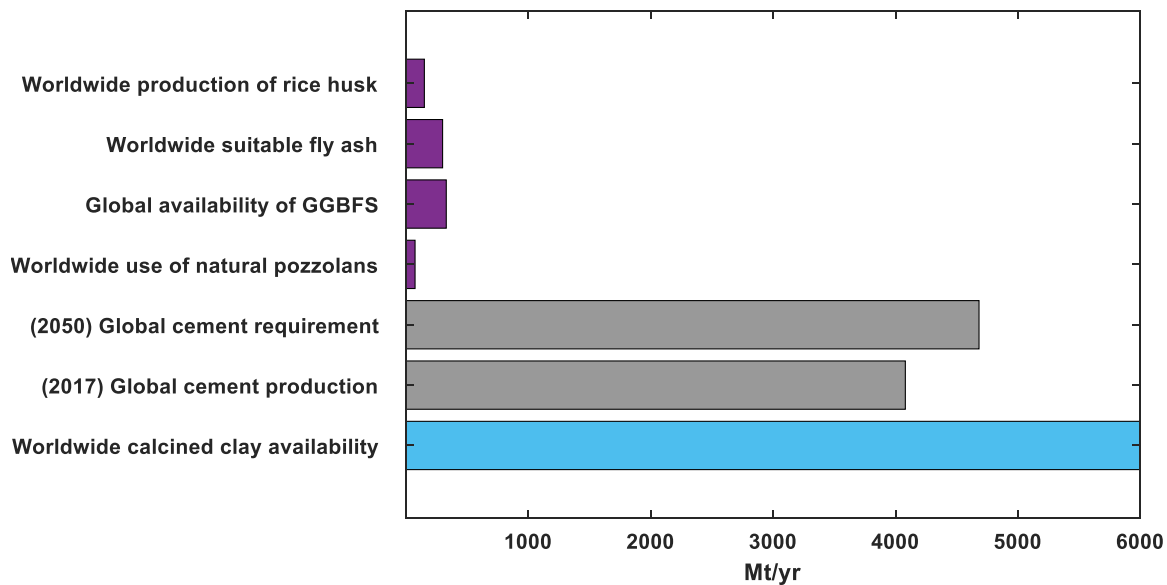
**Figure 1.4** – Evolution in CO<sub>2</sub> emissions from cement production (line with green markers) compared to the annual percentage of clinker used in typical concrete mix proportions as an indicator of the degree of adoption of SCMs in binders. Data obtained from companies from the “Getting the Numbers Right” GNR – GCCA Database [16]

### 1.1.6.1 GGBFS and Fly Ash

GGBFS along with fly ash are the most common cementitious admixtures used due to their high content of Ca (in GGBFS and fly ash class C), Al, Si and Fe, which are the principal components of cement. These materials are industrial by-products from steel refineries and coal power plants respectively. Since industrial by-products are considered waste from their primary industry, GGBFS and fly ash are considered to have minimal or no allocated impact in the overall GWP of the concrete mix. In Japan in 2008, approximately 49% of slag and 64% of fly ash production was used as SCMs for cement manufacturing [17].

Suitable amounts of fly ash and GGBFS for use as partial replacement of clinker in cement has become scarce within the last decade as these materials come from energy-intensive industries that contribute themselves to high emissions of CO<sub>2</sub> into the atmosphere. The use of fly ash as a SCM in cement is limited due to the decline of coal-fired power plant operations for electricity

generation (i.e. a drop of 13% in coal consumption in the US in 2015) [26] and a shift into natural gas and renewables sources for energy production. A similar scenario is observed for GGBFS, where a shift into more energy efficient technologies for steel refinery has significantly lowered the amount of GGBFS produced as a by-product. In addition, these furnaces are not distributed homogeneously around the world. The implementation of a long-term SCM depends considerably on its local availability, otherwise, procurement and transportation costs, as well as increased emissions from transportation largely offset any potential reduction in CO<sub>2</sub> emissions. As shown in Figure 1.5, shortage of worldwide fly ash and GGBFS (production only covers 8% of the global cement demand [18]), have turned the view of the cement industry into the search of alternative cementitious materials that are more abundant and widespread, with a potential to achieve higher replacement levels and whose calcination temperatures are greatly inferior than that of clinker's.



**Figure 1.5** - Worldwide cement demand and availability of current most-used SCMs. Data derived from: Cement [3, 11], calcined clay, natural pozzolan, GGBFS, and fly ash [15], and rice husk [27]

### 1.1.6.2 Silica Fume

Silica fume is another common industrial by-product obtained from the production of silicon metal alloys. It consists of a very fine and highly reactive silica powder (SiO<sub>2</sub>) whose particles are two orders of magnitude finer than portland cement particles. Its use is focused on special types of concretes such as high-performance concrete whose highly densified matrix allows for early development of strength and for better durability performance compared to normal strength concrete [1]. However, silica fume's very fine composition and its implications on the overall workability of fresh concrete limits its maximum dosage to only 5 to 9% by mass of cement replacement. In addition, availability of silica fume is very limited. Its geographical concentration (where silicon industries are located), and its high cost (\$400 - \$1000 USD per tonne) hinders its wide-scale use as SCM in concrete production.

### **1.1.6.3 Natural Pozzolans**

These SCMs mostly consist of those reactive siliceous materials derived from volcanic rocks. They mainly comprise volcanic ashes (also known as volcanic glass due to its amorphous structure) and are located in areas where volcanic activity is predominant. Another type of natural pozzolans are the diatomaceous earth which are skeletal shells from aquatic algae and are composed of hydrated silica [1]. In general, natural pozzolans do not need activation by heat treatment since they are highly reactive siliceous materials. However, deposits of diatomaceous earth are often found in mixtures with large deposits of clay, hence, they require thermal activation in order to react with lime to form cementitious materials. Availability of natural pozzolans in only few regions in the world limit the widespread use of these materials as partial replacement of cement in concrete. Furthermore, since these materials are naturally sourced, they show a high variability in their reactivity with lime and their angular shape and porosity could sometimes lead to issues in workability [25].

### **1.1.6.4 Rice Husk Ash**

Rice husk is an agricultural solid waste material resulting from the milling process of rice grains during the rice cultivation process. Globally, the production of rice paddy yields approximately 150 million tonnes of rice husk [27, 28] and its disposal could be deflected to the cement kiln to produce suitable ashes that are highly reactive and used as SCMs in blended cements. When rice husk is burnt under controlled environment, the ash that is formed is high in amorphous silica and it has been identified as a suitable, more affordable option than silica fume [29]. When incorporated into concrete mixes with other SCMs, rice husk ash has proven to be beneficial in improving the overall mechanical and durability performance of concrete while reducing the overall CO<sub>2</sub> emissions from clinker production. In a study by Gursel et al [29], quaternary blends of rice husk ash, fly ash, limestone, and portland cement in concrete have proven to have good mechanical performance at later ages (e.g. after 28, 56, and 90 days) while sustaining lower values of GWP than comparable mixes with 100% portland cement. To its disadvantage, rice husk's availability is subject to seasonal and regional availability, hence, it alone, does not meet the global demand for cement substitution.

### **1.1.6.5 Calcined Clay**

Gartner [8] used public US Geological Survey Data to suggest that natural pozzolans such as calcined clays (with high content of Al and Si), are reasonable alternative candidates for cement production. Furthermore, due its widespread localization, calcined clays overcome the issue of ready availability for its use in the future production of cement. In addition, calcined clays have very small CO<sub>2</sub> emissions associated with mining, and calcination of these materials is undertaken at lower temperatures than clinker, making them an excellent low-CO<sub>2</sub> alternative to portland cement.

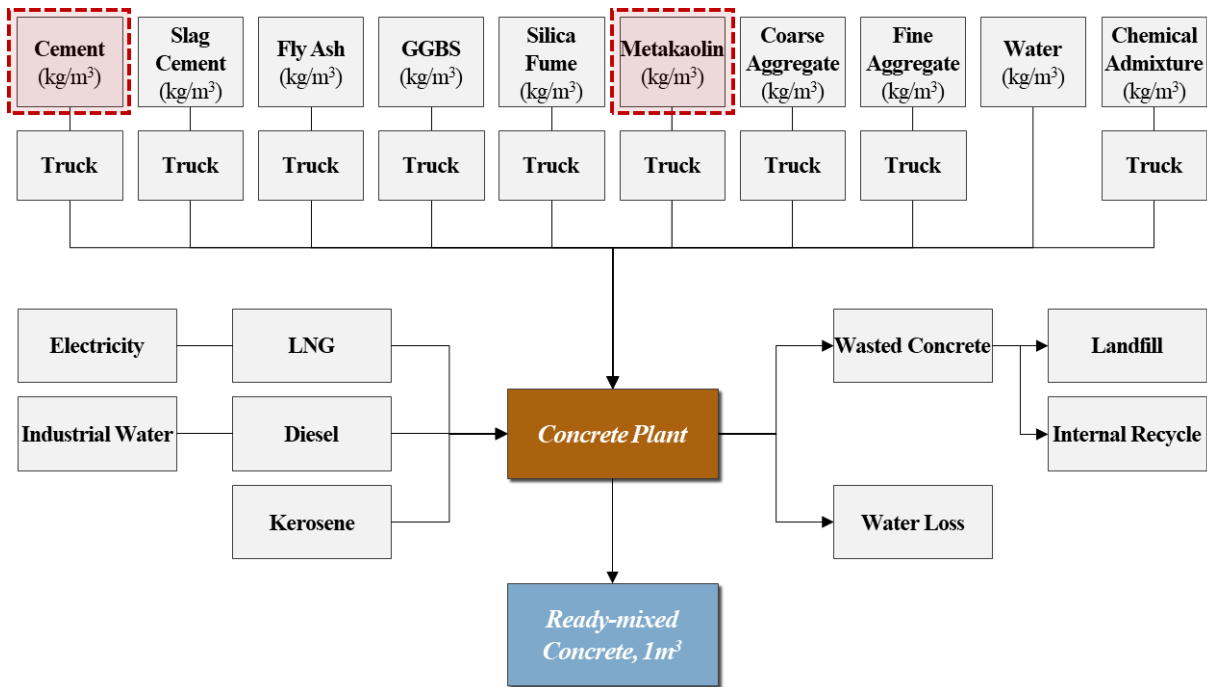
Among all clays, those rich in kaolinite mineral have proven to be more reactive when mixed with cement and limestone [30]. Kaolinitic clays that have been calcined to gain reactivity are also known as metakaolin clays. In this dissertation, I focus on the use of metakaolin and its potential use as an SCM, hence, the terms calcined clay and metakaolin will be used interchangeably in this document.

The interaction of calcined clays with other raw materials such as limestone has also been studied to further reduce the environmental footprint of cement. Researchers consider that the best

attribute of calcined clays in cement comes from its synergic effect with clinker when unburned limestone is added in small percentages [31]. This refers to the ability of calcined clays to react with the calcium hydrates of cement and with limestone to form carboaluminate phases that have shown improvement in the mechanical properties of cement pastes.

An analysis of the mechanical performance reported as well as the interaction of calcined clays in cement when coupled with limestone have shown the potential of this alternative material as partial clinker replacement. Successful industrial trials involving the production and use of calcined clays in cement blends have been done in Cuba, and India [32] and are currently under development in other emerging countries. The best attributes of calcined clays are: their geographical and abundant availability —specifically in developing countries where the need for construction is projected to grow in the next 50 years; the ease of adoption since these materials can be processed in existing kilns in cement plants with little modifications; the ease of implementation by unskilled workers; the reduction in energy costs due to lower activation temperatures; and their excellent interaction with limestone in ternary blends which further reduce the clinker to cement ratio.

Figure 1.6 details each of the main mixture components involved in concrete production as well as their main energy and materials inputs and outputs along the manufacturing process. Cement and metakaolin are highlighted to indicate the focus of this dissertation. Chapter 2 presents a new interpretation of the state of the art of calcined clay's application in cement and concrete. The analysis of their pozzolanic characteristics, thermal treatment, mechanical and environmental performance is discussed based on the latest findings in literature. Chapter 3 presents the experimental work to study the effect of the metakaolin to limestone ratio on the mechanical and durability performance of calcined clay cements in mortar and concrete. Chapters 4 and 5 contain a thorough description of the MKC-LCA Tool that I have developed and its application in the evaluation of the global warming potential of metakaolin production, respectively. Finally, Chapter 6 presents concluding remarks and future work.



**Figure 1.6** - Inputs of energy and resources in concrete production. Includes the most common SCMs incorporated at the concrete production stage. This dissertation focuses on the production process of metakaolin as a potential SCM.

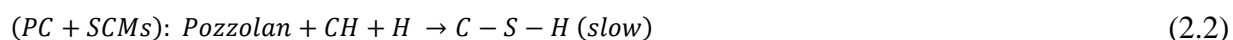
## Chapter 2 – Potential Use of Calcined Clay as Supplementary Cementitious Material

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The following section provides a new interpretation of the state of the art found in available literature. For this work, over 100 publications related to the study of calcined clay in cement, its application, mechanical and durability performance, and interaction with other raw materials as well as its environmental impact compared to ordinary portland cement were carefully reviewed and analyzed in the following sections.

### 2.1 Thermal Treatment and Analysis of the Pozzolanic Characteristics of Calcined Clay

Calcium silicate hydrates (C-S-H) are the main hydration products responsible for the strength and mechanical performance of cement in concrete. However, when substituting clinker for SCMs (e.g., silica- and alumina-rich pozzolans), the C-S-H that is formed is different from that produced when only portland cement is used the binder. Generally, a PC hydration reaction is faster than one when a pozzolanic material is incorporated. Equations (2.1) and (2.2), show the chemical reaction of the two hydration processes<sup>2</sup>.



As discussed in Chapter 1, pozzolans are typically used as partial substitution of clinker in mortar and concrete mixes. In contrast to natural pozzolans and silica-rich by-products (e.g., fly ash and silica fume), clays in their natural state are not reactive with cement's hydration products. For these reasons, it has been of special interest to study the optimal temperatures at which different clays show high reactivity when interacting with clinker and gypsum in cement pastes and mortars. Thermal activation of clays can be obtained at much lower temperatures than that of clinker calcination, thus a substitution using clays may potentially reduce CO<sub>2</sub> emissions. In addition, clay deposits are immensely abundant in the earth's crust, thus, determining which clays are more suitable as supplementary cementitious materials is essential.

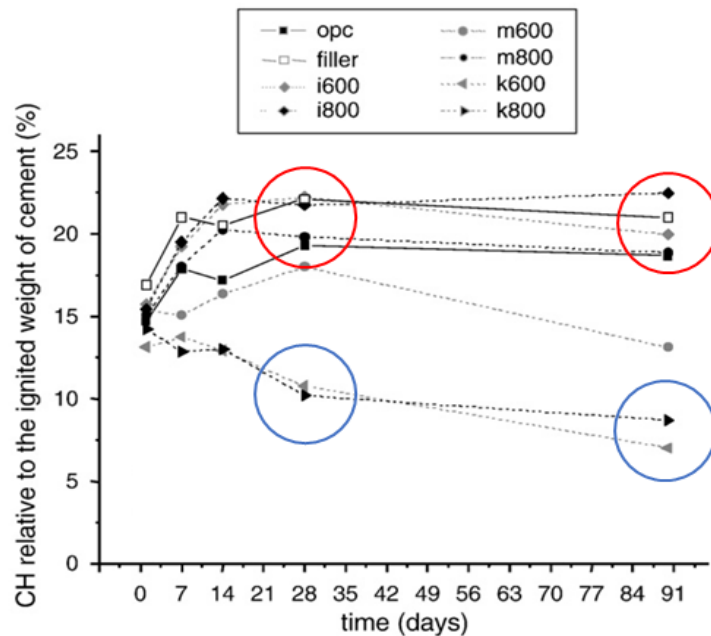
Several studies on the optimal temperature range for thermal activation of clay samples have been carried out using different types and grades of clays. Thermal activation of clays is necessary to obtain a disordered microstructure (dehydroxylation) that provides with pozzolanic characteristics to make them suitable to react with portland cement. The study of CH evolution is a common method to evaluate the efficacy of a pozzolan at reacting with CH to form cementitious materials. Fernandez et al. [13] studied the influence of temperature in kaolinite, illite and montmorillonite (three of the most widely abundant clays on earth) and the influence of thermal activation in the mechanical and physical properties of blends comprising these clays in cement

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<sup>2</sup> C corresponds to CaO  
S corresponds to SiO<sub>2</sub>  
H corresponds to H<sub>2</sub>O

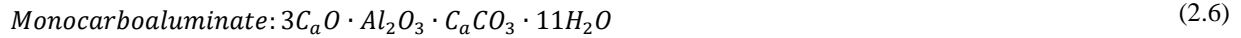
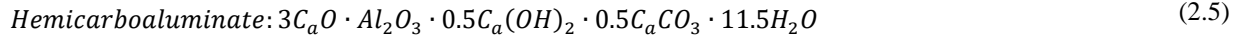
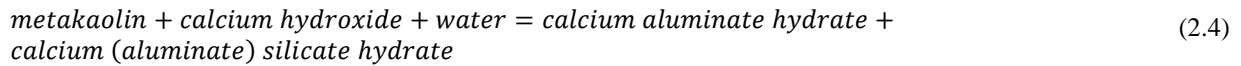
paste. When clay minerals rich in kaolinite are calcined, their crystal structure collapses into a more reactive material called metakaolin ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  or  $\text{AS}_2$  in cement notation) [33]. Under controlled conditions at laboratory scale, kaolinite has been the most reactive of the clays tested, whose dehydroxylation was complete at  $600^\circ\text{C}$ . However, for illite and montmorillonite, loss of crystallinity was not widely observed with thermal treatment, even with the loss of their hydroxyl groups at higher temperatures (i.e.,  $800^\circ\text{C}$ ). The conservation of the crystal structure of illite and montmorillonite, even under high temperatures, hinders the breakdown of alumina and silica from these clays under the interaction with cement's alkaline medium. In addition, other physical properties such as specific surface, particle size distribution and bulk density were negatively affected by thermal activation of illite and montmorillonite. Heat treatment of these clays favors the agglomeration of particles, which results in decreasing the specific surface of the mineral.

This behavior was not significant in kaolinite samples which presented the greatest pozzolanic activity as verified by the large reduction of CH even at early ages. From Figure 2.1 one can observe that kaolinite has better performance in consuming CH from cement hydration as it is shown in the blue circled areas at 28 and 90 days; whereas illite and montmorillonite at  $800^\circ\text{C}$  showed no chemical interaction with PC given that CH content was higher than that of the reference portland cement paste at all ages (red circled area).

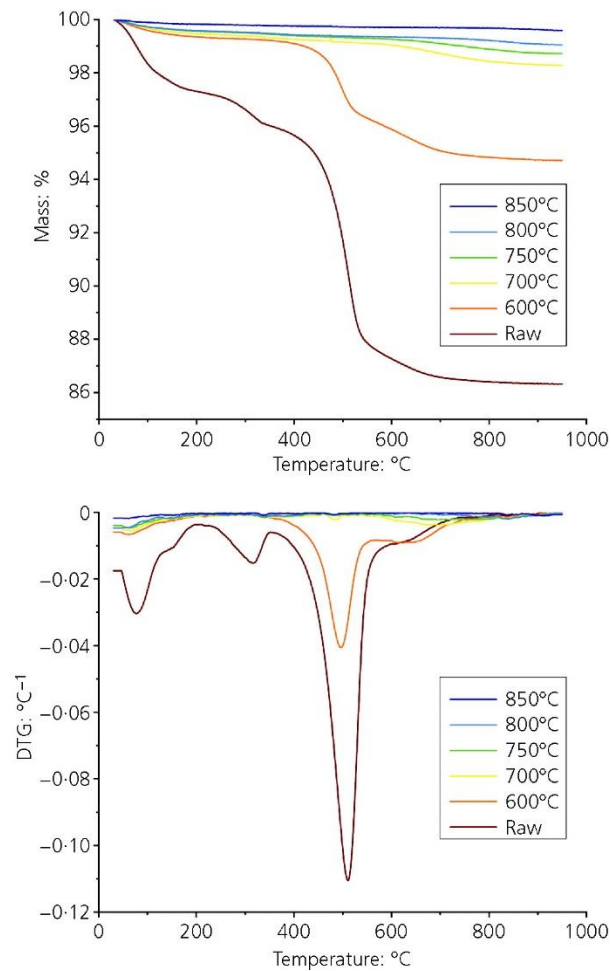


**Figure 2.1** - Calcium hydroxide evolution for cement and blend pastes. Adapted from [13]

Regarding MK, its pozzolanic reaction with portlandite produces C-S-H gel containing alumina and crystalline calcium aluminate and calcium aluminate-silicate hydrates as described in Equation (2.3). When unburned limestone is introduced in the cement blend, the alumina from MK reacts with the calcium carbonate from limestone to yield alumina phases (equations (2.5) and (2.6)) and compounds of calcium and alumina silicates [34, 35].



In a recent paper by Scrivener et al. [36], batches of clays with 50% kaolinite content were calcined at several temperatures between 600°C and 850°C in a static oven. The results from thermogravimetry analysis (TGA) and derivative thermogravimetry (DTG) in Figure 2.2 indicated that clays with this percentage of purity showed a partial dehydroxylation at 600°C with a complete activation at 700°C.

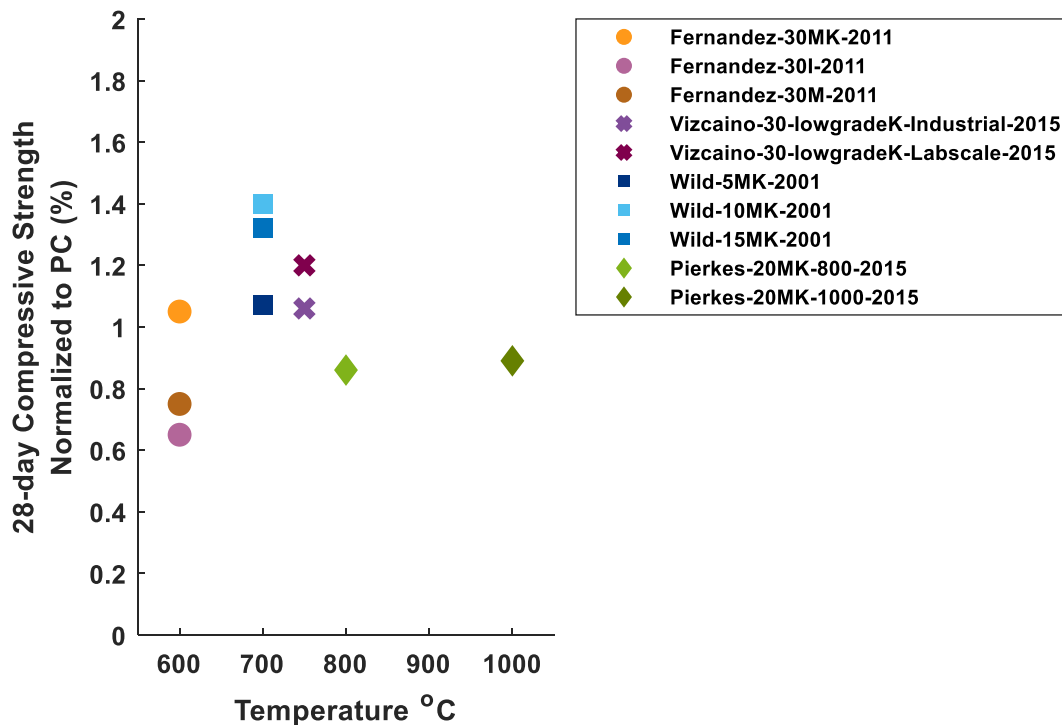


**Figure 2.2** – TGA and DTG results from calcined clay with 50% kaolinite at different temperatures of calcination. Figure from [36]



The complete calcination measured by TGA and DTG does not fully establish the optimal temperature of calcination for the metakaolin to be at its most reactive state when used as a SCM. Additional tests to assess the pozzolanicity of the MK were performed by the authors. The heat release by isothermal calorimetry was monitored for the first day of hydration of cement blends with MK and limestone. Results showed that the highest heat released corresponded to the blends whose batches of clay were calcined at 800°C, which is 100°C higher than the complete dehydroxylation registered by TGA and DTG (i.e., 700°C). The authors also suggested that higher temperatures of calcination (i.e., higher than 850°C) rendered the MK particles coarse which decreased their reactivity with portland cement [36].

Compressive strength is an indirect measure of the pozzolanic activity of the calcined clay in the blend which helps in understanding the pozzolanic characteristic of calcined clays. Figure 2.3 compares different temperatures of calcination of clays and their relative compressive strength in mortars at 28 days. Vizcaino et al. [34] studied ternary blends with limestone and a kaolinite clay with low content of kaolinite mineral (i.e., low-grade) which was calcined at around 750°C. These blends showed better mechanical performance than dual blends from Fernandez et al. [30] which had the same replacement level of 30% metakaolin but used high purity kaolinite clay. Despite the low quality of the kaolinite used by Vizcaino et al., both studies confirmed that of all the types of clays analyzed, those containing kaolinite mineral are considered the most reactive and pozzolanic.



**Figure 2.3** - Influence of calcination temperature on the mechanical performance of cement blends with different SCMs and different clinker factors. Results are normalized to PC at 28-days. MK (metakaolin); I (illite); M (montmorillonite); LowgradeK (low grade Kaolinite).

In addition, the pozzolanicity of these blends under full scale production proved to be efficient and showed similar values of compressive strength as portland cement, suggesting its feasibility for mass production. Vizcaino et al. [34] studied ternary blends composed of low-grade kaolinite clays, unburned limestone, and PC that were industrially manufactured. A full-scale trial was conducted at a cement plant in Cuba in which an outdated wet rotary kiln was modified to allow for clay calcination in a dry state. The temperature used for thermal treatment of the clay selected was 750°C. For this trial, the clay deposit chosen consisted of medium-grade kaolinitic clay with 48.6% kaolin mineral. The authors' scope was to assess the feasibility and performance of these types of blends when produced in real conditions. Comparisons of the pozzolanic activity of this industrial batch with portland cement and a typical commercial blend produced under laboratory conditions were also assessed by the author and it is reviewed in the following Section 2.2.

## 2.2 Mechanical Performance of Calcined Clay Cements

### 2.2.1 Assessment at Laboratory Scale

Strength development and water demand are often the limiting factors in the amount of replacement of PC with SCMs. Table 2.1 shows the specified limits of percentage savings in clinker of different SCMs according to ASTM C595 [37].

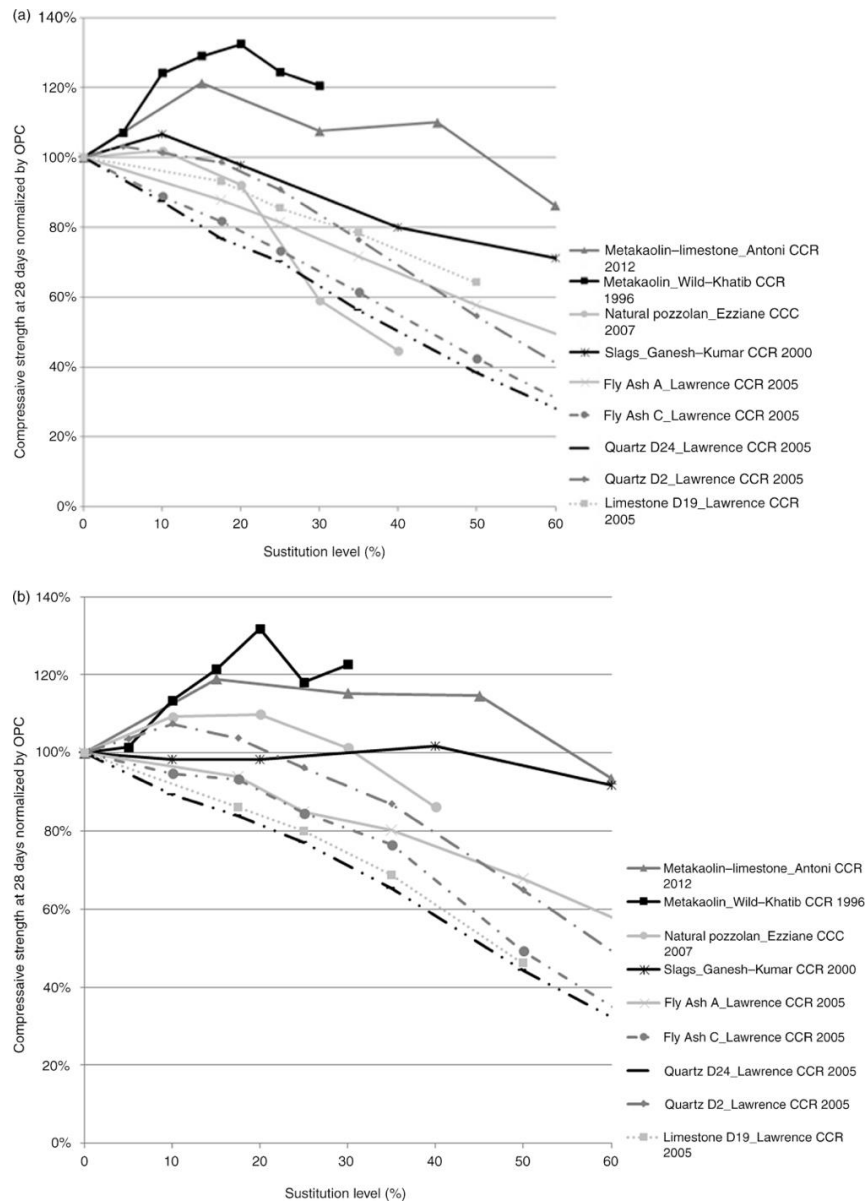
**Table 2.1** - Specification limits for different Supplementary Cementitious Materials according to ASTM C595 [37].

| Constituent               | Spec. limits % savings in clinker (by mass) |
|---------------------------|---|
| Natural Pozzolan          | Up to 40                                    |
| Fly Ash Type C            | 50-70                                       |
| Fly Ash Type F            | Up to 40                                    |
| Slag                      | 70-95                                       |
| Silica Fume               | 5-10  |
| Limestone                 | 5-15  |
| Limestone + Calcined Clay | Up to 15; Up to 40                          |

From this group of blended cements, ternary blended cements that incorporate clinker with the addition of unburned limestone and alumina-rich pozzolans (e.g., calcined clays) have been studied in recent years [38-42]. This particular combination has proved to perform closely to PC as early as 7 days [42]. The addition of limestone not only enhances the mechanical properties of hardened concrete, but also improves the rheology of fresh mixes. Calcined clays normally require larger amounts of water than regular PC, limiting its percentage of cement replacement. With the addition of small percentages of limestone, it becomes feasible to aim for higher substitution levels of cement without compromising workability of the mix [43].

The potential use of metakaolin as a SCM is not only based on their widespread availability [44], but also in their efficiency to replace clinker without compromising performance and

durability. Even though the reaction of pozzolanic cement blends is slower than cements containing 100% PC, these substitutions have shown a general pattern of enhanced mechanical properties of cement pastes at later ages. The strength development in cements containing SCMs becomes visible after 28 days and it normally outperforms that of PC at 56 and 90 days [1]. An improvement of strength in the long-term is developed since the reaction of pozzolans with calcium hydroxide contributes to pore refinement and densifies the cement-aggregate interface, reducing the flaw size distribution. Vizcaino-Andres et al. compared in Figure 2.4 the compressive strength of different alternatives for blended cements with different clinker factors and normalized to the 28-day strength of PC [34]. Ternary blends of metakaolin (MK) and limestone show higher compressive strength than PC even at a 45% substitution level. Similar behavior is observed for slag blends with 40% replacement of clinker.



**Figure 2.4** - Compressive strength of blends made with various SCMs at different substitution levels normalized to PC a) 7-day and b) 28-day. After Martirena-Hernández, et al. and references therein [34]

Antoni et al. (2012) [42] studied the compressive strength at 1, 7, 28, and 90 days of 10 mortars made of single substitutions of quartz at 15, 30, 45, and 60% of replacement level; single substitution of limestone at 15%; single substitution of metakaolin (MK) at 30% and coupled substitution of MK and limestone (2:1 ratio) at total levels of 15, 30, 45, and 60%. Figure 2.5 shows the relative compressive strength of all the mixes compared to that of the reference PC mix. Several remarks are highlighted by the authors. Blend 15 (B15) with 5% and 10% of limestone and MK respectively, has higher compressive strength than PC at all ages. In addition, blends B30 with 10% limestone and 20% MK replacements, and B45 with 15% limestone and 30% MK showed higher strength than PC at 7 and 28 days. In these ternary systems, the alumina phases appear to react faster than mixes only containing MK and clinker (e.g., from this study, when comparing the single replacement of 30% MK mix with the B45 blend, the CH consumption after 1 day is stronger than that of MK30 mix, based on thermogravimetric analysis). Substituting cement for limestone is also cheaper and significantly improves the workability and water demand of the mixes compared to those only containing MK replacement [31].

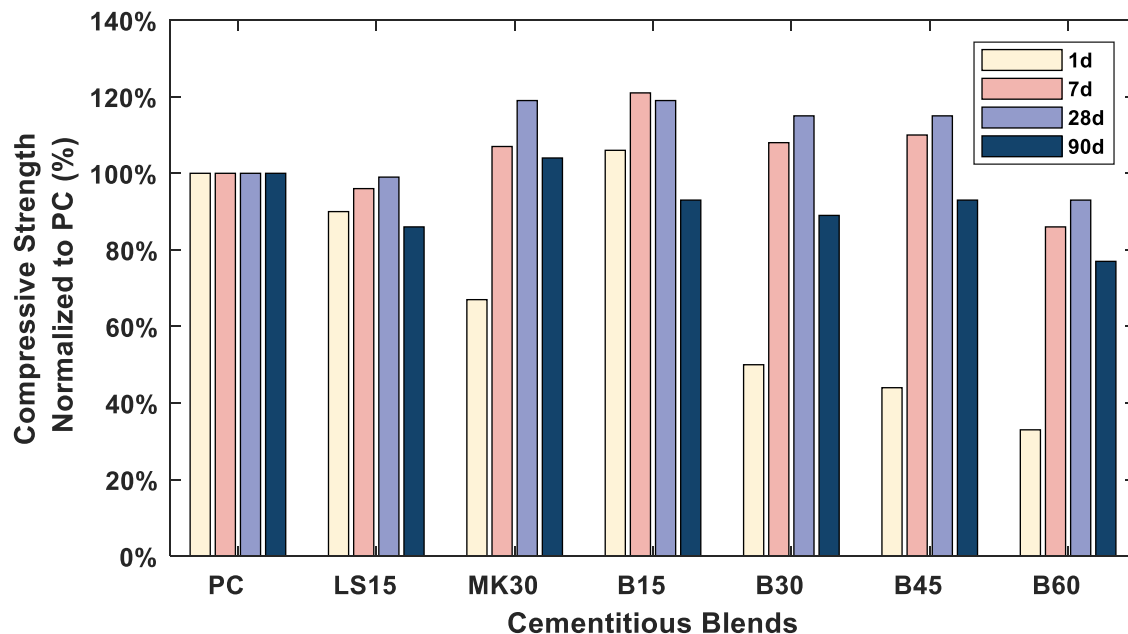


Figure 2.5 - Compressive strength of cementitious blends normalized to the strength of PC. Adapted from [42]

Concrete mixes with metakaolin and limestone (50% clinker replacement with 31% MK, 15% limestone, and 4% gypsum) were studied by Dhandapani et al. [45] and compared to mixes of 100% PC and pozzolanic cements with fly ash (30% substitution level). The evolution of strength was studied on concrete cubes with a target strength at 28 days of 30 and 50 MPa, and samples of a common mix that contained the same w/b ratio and a constant binder content. Results for the groups with the same strength grade showed that compressive strength of the mixes containing MK and limestone were comparable to those containing only PC at 28 days with a further increase in strength at later ages. Similar results were found with the mixes containing fly ash. However, the principal difference was the lower strength values registered at earlier ages (i.e.,

less than 28 days) for those mixes compared to the ones with MK and limestone and the ones with 100% PC. For the mixes with same binder content and w/b ratio, mixes with MK and limestone showed higher values than those with pure PC and those with fly ash replacement at all ages analyzed. In concrete mixes, the addition of metakaolin contributes to the overall strength of the mix by accelerating the hydration of PC at early ages in contrast to other SCMs; consuming portlandite in the pozzolanic reaction to form more cementitious phases; and densifying the matrix due to its filler effect [33]. In addition, the authors studied the static elastic modulus of concrete cylinders made with the same concrete mixes. Systems with MK and limestone showed similar elastic moduli than those from 100% PC and from the blends with fly ash, indicating the feasibility of cements with MK and limestone to perform adequately in structural applications.

Akindahunsi et al. [46] examined the suitability of different clay sources from Nigeria as SCMs in cement. The compressive strength of concrete cylinders composed of 50% and 65% clinker replacement with varying grades of kaolinite clays and limestone (namely LC<sup>3</sup>-50 and LC<sup>3</sup>-35) was assessed. The ratio of calcined clay to limestone used in the concrete mixes was 1:1. The percentage of kaolinite mineral in the clays selected was determined to be 32% and 52% respectively. Strength results after 7 days were similar to that of PC for both LC<sup>3</sup>-50 blends despite of the different content of kaolinite in the raw clays and the pattern was maintained constant after 28 days. After this age, the mixes made of clays with 52% kaolinite content surpassed the compressive strength of PC. Even though LC<sup>3</sup>-35 concrete's strength values were lower than that of PC after 28 days, the difference in strength was not significant (i.e., 18%) considering the low grade of kaolinite used (i.e., 52%) and the high dosage of PC replacement (i.e., 65%). The elastic moduli of all three LC<sup>3</sup> mixes studied were very similar to that of PC concrete (average elastic moduli of 28.75 GPa) even for those mixes with high replacement ratio (i.e., LC<sup>3</sup>-35), indicating their feasibility to be used as SCMs in concretes without compromising the composite's structural performance.

Yu et al. studied the performance of mortars made of cement with blends of limestone and metakaolin at levels of 25%, 50%, 60%, 70% and 80% by weight of total binder. The compressive strength of these mortar cylinders was compared to mortars made with the same replacement levels of cement with fly ash and with a mortar made with 100% PC as the benchmark. Results showed that those mortars made with limestone and MK achieved higher early (i.e., 3-day and 7-day) compressive strength values even for higher dosages of replacement (i.e., 50%, 60%, and 70%) after 28 days. In addition, the strength evolution from age 3-day to 7-day was higher for blends of MK and limestone than for blends containing fly ash, and those containing fly ash at high replacement levels showed lower performance than plain portland cement mortars at the same early ages which indicates the higher performance of MK and limestone as SCMs in the early strength development. Furthermore, compared to PC mortars, those with replacement ratios of 50% and 60% with metakaolin and limestone showed comparable compressive strength values at 28 days confirming the suitability of MK and limestone at high levels of replacement [47].

### **2.2.2 Assessment at Industrial Scale**

A serious mitigation strategy to reduce cement's environmental impact has to be both feasible and replicable at industrial scale without compromising performance. Industrial production of cement blends with calcined clay has proven successful at industrial scale in different regions of the world [34, 48-51]. Ternary blends with substitution of 50% of the mass of clinker by limestone and calcined clay in Cuba have shown positive correlations between compressive strength values of

the batches developed in the cement plants and those produced under laboratory conditions. The industrial trial was developed at a cement plant in Cuba as part of the Limestone Calcined Clay Cement (LC<sup>3</sup>) project in conjunction with the Swiss Development and Cooperation Agency [39]. The industrial manufacturing of 130 tonnes of cement contained 50% of clinker, 30% of medium-grade kaolinite clay (48% content of kaolinite), 15% limestone and 5% gypsum. The trial included the calcination of approximately 110 tonnes of clay in dry conditions at 750°C using a decommissioned wet rotary kiln. The calcined clays were further co-ground in a ball mill with double chamber and mixed with limestone, clinker, and gypsum. The compressive strength of standardized mortars was assessed and compared with 100% PC and ternary blends of the same mix proportions elaborated under controlled laboratory conditions. The results showed comparable strength values among the industrial batches of ternary blends and those made at small scale in the laboratory. Moreover, all of the ternary blends (i.e., industrial batches and laboratory samples) were superior than those made of PC after 3 days, thus, proving the feasibility of the industrial process. Batches of the ternary blends produced in the plant were distributed to manufacturers of building materials in order to produce hollow concrete blocks (500x200x150mm) and 25 MPa precast concrete elements following the same procedures and proportions that are usually implemented by these plants when using portland cement. Results of mechanical strength of both applications following Cuban standards showed that this ternary blend is suitable to replace portland cement for the industrial production of these structural elements (See Table 2.2).

**Table 2.2** - Results of compressive strength of concrete elements made with ternary cement blends under industrial trial. After Martirena-Hernández, et al. [34]

| <b>Application</b>             | <b>Material</b>                | <b>Average compressive strength at 28 days (MPa)</b> |
|--------------------------------|--------------------------------|--|
| Hollow blocks (500x200x150 mm) | Ternary blend                  | 5.9  |
|                                | PC (specification NC 247:2010) | 5.0  |
| Precast elements               | Ternary blend                  | 31.4   |
|                                | PC                             | 33.2   |

Reduction in costs of production is also a positive outcome from the use of calcined clays with clinker to produce blended cements. Given the location of the clay deposits, extraction of suitable clays could have less monetary impact than the extraction and transportation of conventional raw materials for cement production. In addition, operational costs from cement manufacturing (e.g., grinding, mixing, pyro processing, and cooling) also showed relatively high savings in industrial trials conducted in Cuba [34, 41].

It is worth noting that lower grade kaolinite clay is readily available and does not have market competition due to its low quality. In addition, this material can be processed using the same infrastructure available for cement production with only minor changes, requiring minimal capital investments. Long-term industrial production of calcined clay in cement plants can provide higher energy savings and environmental advantages compared to PC. This solution becomes more

attractive when high investment costs associated to the improvement of kiln technology is a limitation.

Successful trials of LC<sup>3</sup> production were conducted at three different sites in India between 2014 and 2017 and reported by Krishnan et al. [49]. For these trials, the production of limestone calcined clay cements was carried out using different calcination equipment (i.e., static and rotary kilns) and different grinding methods (i.e., open- and closed-circuit ball mills) to compare the efficiency of the process and the quality of the final product with different technologies available at each cement plant. In parallel to the manufacturing process, different sources of raw material (i.e., different clays, clinkers, and limestones) were used to determine the suitability of local raw materials in the production of LC<sup>3</sup> at large scale. For all three trials, the LC<sup>3</sup> cement comprised 50% clinker, 30% metakaolin, 15% limestone, and 5% gypsum. Four clays (i.e., K1, K2, K3, and K4) sourced from different locations in India were selected to analyze their feasibility as SCMs in cement blends with limestone. XRD and TGA tests were performed on all clays to characterize their mineral composition. One of the clays (K1) was considered to have high content of kaolinite and even though higher content of this mineral enhances cement's mechanical performance, medium- and low-grade clays proved successful in providing comparable strength values without sacrificing durability performance. LC<sup>3</sup> blends with a fixed w/b ratio of 0.45 were studied with clays of different kaolinite content (K1 with 86.4% and K3 with 58%). Results showed that blends made with K3 performed better than those made with K1 (28-day strength of 43 MPa vs 39 MPa approximately) despite the lower kaolinite content of K3. Both blends however, showed very similar results than those of blends made with 100% PC. Industrial calcination was considered by means of static and rotary calciners. Static calciner was not advised given that calcination was not uniform and only 50% of the total mass of clay was properly calcined. In addition, the effective temperature measured at each of the containers holding the raw clays was significantly lower (450°C) in comparison with the temperature of the air inside the calciner (1100°C). Long residency time for proper calcination and slower turnaround of product due to high down times from loading and unloading of the clay in and out of the calciner did not render the static calciner as the most cost-effective method for clay calcination in LC<sup>3</sup> production at industrial scale. On the other hand, calcination via a rotary kiln was conducted successfully with a residency time of approximately 20 minutes for each batch of clay. The optimum temperature for complete calcination on the clay fed in the kiln was determined to be 950°C which is naturally higher than the range of 650°C to 800°C reported from TGA results and previously assessed at laboratory scale with significantly smaller amounts of clay.

Interestingly, variations in the mineral composition and quality of the raw materials did not only focus on the kaolinitic clays. Various sources of carbonates (i.e., high grade limestone, dolomitic limestone, dolomite, and marble dust) with varying compositions were also incorporated into different mixes of the same w/b ratio and composition to form LC<sup>3</sup> blends. The authors showed that regardless of the carbonate source, the LC<sup>3</sup> system had comparable results of compressive strength to those of PC blends. This result emphasized the robustness of LC<sup>3</sup> and its feasibility of application in areas where high-grade limestone is limited and exclusively utilized for clinker production.

The authors also suggested that calcination was not the only production process where variations reflected some difference in the quality of the final blended cement. After calcination, clinker is typically blended and ground simultaneously with gypsum (i.e., interground) to produce

portland cement. However, when softer materials such as limestone and calcined clay are incorporated to produce blended cements, specially at high dosages of replacement, the harder clinker could not be fully ground (i.e., undergrind) due to the preferential grinding of the softer clays and limestone, which in turn are overgrind as a result. The resultant blended cement is poorly graded, and could render unworkable at the fixed water-to-binder ratio (w/b). In addition, coarser clinker particles could hinder the hydration processes which in turn delay the pozzolanic reaction of the calcined clays. To overcome this problem, individual grinding of each component could be followed by interblending of the cement, limestone, and calcined clay without compromising performance. However, the authors suggested that in the Indian context, the intergrinding of raw material remains the most viable method of grinding the cement at industrial scale. In specific, intergrinding via closed-circuit ball mill was recommended. LC<sup>3</sup> cements produced during these industrial trials were successfully used for the construction of a two-story building and for the industrial manufacture of concrete paver blocks and autoclaved aerated concrete blocks with only minor modifications in the mix designs and compliant to national standards.

### **2.3 Durability Performance of Calcined Clay Cements**

As discussed in Section 2.2., blended cements with a partial replacement of cement with MK and limestone have proven successful in terms of their compressive strength when compared to PC blends in mortar and concrete applications. However, performance of different binders is also related to the capacity to retain their mechanical properties during their service life and when exposed to harsh environmental conditions and aggressive solutions. Much of the success of concrete's service life is directly related to the properties of cement's transport mechanisms and the permeability of the matrix. In general, a denser matrix would render difficult the free transport of harmful ions that diffuse from the surface of the concrete cover. Recent studies on durability of calcined clay cements under different scenarios is discussed herein.

#### **2.3.1 Behavior under Chloride Induced Corrosion**

Corrosion of steel rebar that is embedded in concrete often occurs due to the ability of chloride ions from ocean water or de-icing salts to penetrate through the concrete. This causes depassivation of the rebar which could lead to corrosion and potential rebar mass loss, concrete cracking, and a subsequent reduction in the structural capacity of the composite member [52]. Corrosion of steel comprises an oxidation-reduction reaction in which the steel upon depassivation, loses electrons (anode) and the water and oxygen present in the pore solution (cathode) consumes these electrons and interacts with the now ionized metallic iron to form rust products (e.g., iron oxides and iron hydroxides). These new products are far more expansive than the original metal [1]. Given that this process is controlled by the ability of water and oxygen in the pore solution to consume electrons, permeability of the cementitious matrix is a key factor to control the rate of corrosion in reinforced concrete.

Concrete with low permeability is usually achieved with a low water to binder ratio, a well graded distribution of aggregates, and the use of SCMs. The potential of corrosion of the steel embedded in concrete containing blended cements with MK is reduced due to the interaction of two phenomena: the pore refinement that occurs when MK is added to portland cement in concrete which reduces the overall permeability of the matrix, and the increased capacity of chloride



binding which slows down the diffusion of chloride ions, hence, reducing their concentration in the pore solution, and delaying the corrosion initiation stage.

Shi et al. [53] investigated the chloride profile of mortars containing binary cement blends with limestone, and metakaolin, a ternary cement blend with a combination of both metakaolin and limestone, and a quaternary cement blend with metakaolin, silica fume, and limestone. The replacement ratio of 35% by weight of cement with SCMs was studied across all combinations with a constant water to binder ratio of 0.5. To assess chloride resistance, one end of the mortar cylinders was exposed to 700 mL of a 2.8 M NaCl solution during 35 days when layers of the exposed surfaces were collected and the total chloride concentration in the collected powder samples was measured by titration. All of the mortars containing MK showed lower chloride content and shallower penetration depths than those made with 100% PC and a blend of PC and limestone. The latter being the mortar with the highest amount of chloride across all of the blends studied which is explained by the higher permeability and higher porosity of the limestone blends observed in the mercury intrusion porosimetry tests (MIP). In a more recent study by the same authors [54], the chloride binding properties of MK in portland cement blends were identified to come from two different mechanisms: a chemical binding of chloride ions and the aluminates of MK to form Friedel's salt (i.e.,  $\text{Ca}_4\text{Al}_2(\text{OH})_{12}\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ ) and a physical binding of chloride ions that are adsorbed in the diffuse layer of C-S-H.

Dhandapani et al. [45] reported the performance of several concretes made with a ternary blend of PC with limestone and metakaolin compared with those made with 100% portland cement and blended portland cement with fly ash. Three different concrete mixes, two targeting specific compressive strength values of 30 and 50 MPa at 28 days respectively, and one using the same water-binder ratio (w/b) and binder content were subjected to different tests (i.e., resistivity of concrete, resistance to chloride ingress, gas permeability, and water absorption and porosity) to assess their transport properties. Resistance to chloride penetration tests (RCPT) and accelerated chloride migration tests were performed in all of the mixes. RCPT gives a qualitative assessment of the concrete's resistance to chloride ingress by measuring the total charge passed through a concrete cylindrical disk of 100 mm diameter and 50 mm thickness. The results at 28 and 90 days showed that for all of the concrete mixes with metakaolin and limestone had minimal charge passed falling into the "negligible" category according to the ASTM C1 202 standard, whereas concretes with fly ash showed only "very low" resistance to chloride penetration at later ages (i.e., 90 days). This result confirms that metakaolin and limestone contribute to the formation of secondary hydration products that lead to a pore refinement at early ages in contrast to the mixes containing fly ash. Furthermore, chloride migration tests showed that lower non-steady state chloride migration coefficients were identified for those concretes containing MK and limestone regardless of strength class and w/b ratio in contrast with PC concretes and those containing fly ash, even at early ages (i.e., 28 days) supporting the findings from the RCP tests. Results from the RCPT showed a good correlation with the results from the concrete resistivity tests which measured the electrical resistance of the sides of the saturated concrete specimens as an interpretation of the pore connectivity and its resistance to ionic ingress. Other work supporting these findings was done by Maraghechi et al. [55] who analyzed the chloride transport properties of  $\text{LC}^3$  with various kaolinite contents. From their study, the authors concluded that clays with intermediate content of kaolinite mineral (40-50%) were enough to reduce the diffusivity of the matrix by two orders of magnitude compared to PC, thus, demonstrating the applicability of a wider range of clays with kaolinite contents lower than 95% (high purity, expensive) kaolinite

clay. Ultimately, even though the pH of the pore solution in cement blends with MK is reduced with the consumption of CH, the rate of chloride binding and the reduction in permeability protects the overall concrete from chloride-induced corrosion in reinforcing steel.

### **2.3.2 Behavior under Sulfate Attack and Alkali Silica Reaction (ASR)**

Sulfate attack is a chemical reaction that originates from the interaction of sulfate ions with hydrated portland cement which in turn forms more expansive products that produce internal stresses and displacements leading to concrete deterioration and failure. Upon concrete cracking, more contaminants can percolate inside the concrete matrix and continue the cycle of degradation. Sulfate ions can be found in groundwater, agricultural soil, and in sewer pipes. The extent of the damage can be related to the type of cation that is present in the sulfate solution (e.g., sodium, potassium, or magnesium). When sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) is the main sulfate contaminant, the secondary reaction product (sodium hydroxide) continues to provide the high alkalinity of the matrix as it is soluble in the pore solution. High pH is essential in the matrix to stabilize C-S-H. In contrast, under potassium sulfate attack ( $\text{MgSO}_4$ ), the reaction leads to the conversion of CH to gypsum with magnesium hydroxide as the by-product. Magnesium hydroxide is insoluble in the pore solution, hence, reducing the pH of the medium and rendering CSH unstable and prone to react with more potassium sulfate and compromise to a bigger extent the integrity of the system [1].

SCMs in blended cements have been studied under the exposure to sulfate solutions and have proven to be more resistant to sulfate attack than cements with pure portland cement. Mortar prisms made with limestone and metakaolin were exposed to a  $\text{Na}_2\text{SO}_4$  solution and their length and weight were measured every week during one year by Shi et al. [53]. Mortars made with only PC and those made with PC and limestone exhibited poor resistance to sulfate attack and showed significant expansion compared to the rest of the mortars containing MK, including those that contained a combination of MK and limestone. In fact, mortars containing MK showed a decreased in mass with time which the authors correlated to leaching of the cement hydrates. Shi et al. later concluded in [56] that the pozzolanic reaction of MK and the dilution of the cement phases due to the addition of limestone reduces the amount of calcium available in the matrix to react with sulfate ions. This reduction in turn, decreases the potential formation of ettringite and gypsum which is the main manifestation of sulfate attack in cement. For this study, mortars with calcined clay (CC) and limestone (L) in a ratio  $\text{CC}/(\text{CC}+\text{L}) \geq 0.5$  subjected to a  $\text{Na}_2\text{SO}_4$  showed excellent sulfate resistance.

Alkali silica reaction (ASR) is another expansive chemical reaction that leads to potential cracking and deformation of hardened concrete. ASR occurs when reactive silica from the aggregate used in concrete mixes reacts with the alkalis from cement hydration (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{OH}^-$ , and  $\text{Ca}^{2+}$ ) and moisture to form expansive products that exert tensile forces in the already hardened concrete. This leads to cracking of the matrix which can increase the path for moisture to ingress and further intensify the growth of the ASR products [57]. Supplementary cementitious materials' consumption of portlandite to form cementitious phases have proven effective in restraining the expansion of hardened concrete that contains highly reactive siliceous sands as fine aggregates [58]. MK is one of the SCMs used to help prevent ASR by reducing the amount of available CH that is consumed in the pozzolanic reaction. The reduction of alkalis hinders the formation of the expansive gel that originates from the reaction between CH and active silica ( $\text{SiO}_2$ ) from reactive sands [33]. Despite of the purity of the MK (i.e., kaolinite content lower than

95%), mortars made with a combination of portland cement, metakaolin, and limestone at different replacement ratios have proven very successful at resisting degradation due to ASR. Scrivener et al. [36] tested mortar bars made of blends composed of PC, MK, and limestone in replacement ratios of 65% and 50% by weight of cement and the reactive aggregate Jobe as fine aggregate. The bars were soaked in a NaOH solution with outstanding results in suppressing expansion compared with those from the bars containing only PC.

### **2.3.3 Behavior under Carbonation**

Portland cement concrete is naturally susceptible to carbonation. This phenomenon is especially relevant for aging reinforced concrete structures exposed to environmental pollution [59]. Carbonation occurs when  $\text{CO}_2$  from the atmosphere interacts with the pore solution of uncarbonated concrete.  $\text{CO}_2$  reacts with portlandite and C-S-H to form  $\text{CaCO}_3$  and amorphous silica which in turn, reduces the pH of the overall pore solution. A decrease in the pH of the medium, causes the depassivation of the embedded rebar, and the initiation of steel corrosion.

Because the use of a pozzolan such as MK reduces the amount of portlandite in the matrix due to both the pozzolanic reaction and the overall lower PC content from the clinker reduction, a drop in the pH of the pore solution is observed. This reduction of the pH renders the concrete more susceptible to carbonation and ultimately, less resistant to corrosion of the reinforcing steel [59, 60]. Shi et al. [61] studied the effect of carbonation in blends containing limestone and calcined clay with high content of kaolinite produced under laboratory conditions. The investigation focused on the changes in the microstructure due to carbonation of concrete made with different cement blends containing 35% replacement by weight of clinker with metakaolin. Especial interest was put into the differences when metakaolin was used as the single SCM and when it was mixed with limestone in the blend. In addition, their behavior under carbonation was compared with concretes made with the same replacement ratio of limestone and those made with only PC. Mortar bars were made with these four blends and exposed to a concentration of 1%  $\text{CO}_2$  by volume under controlled temperature and humidity for up to 280 days. Carbonation depths were noticeable after 7 days only for the mixes containing limestone, metakaolin, and the combination of both. PC mortar showed the highest resistance to carbonation measured by the phenolphthalein spray method and mortar containing limestone as the single SCM showed the lowest resistance and highest carbonation depth at every age studied. Mortars with binary blends with MK and ternary blends with MK and limestone exhibited high carbonation depths similar to those of the mortars with limestone. Higher carbonation resistance of PC mortars is related to the higher  $\text{CO}_2$  binding capacity which causes a slower reduction of the pH, thus, reducing the  $\text{CO}_2$  diffusion into the matrix.

Investigation on the influence of carbonation in concrete with cement blends containing medium- and low-grade kaolinitic clays was done by Mohammad et al. [62]. The authors investigated the carbonation resistance of concretes made with cement blends of limestone and calcined clay (in a 2:1 ratio) at replacement ratios of 30% and 45%. The clays used contained 50% amorphous material. The study determined that replacement of cement with a limestone-calcined clay blend in concrete, provided with an adequate protection against carbonation as long as the total substitution of cement was limited to 30% by weight. This study included accelerated and natural carbonation tests in concretes specimens. It is worth noting that cement substitution with limestone and calcined clay was done at the concrete batching level and no alkali or sulfate optimization was considered. Ultimately, the authors suggested that additional concrete cover

thickness should be considered in the design when using limestone and calcined clay in cement-based concretes in order to guarantee their service life, especially in areas exposed to wet-drying cycles. Carbonation of concrete made with partial replacement of cement with MK and limestone, especially in high dosages, remains an active subject of research.

## 2.4 Environmental Performance and Availability of Calcined Clay

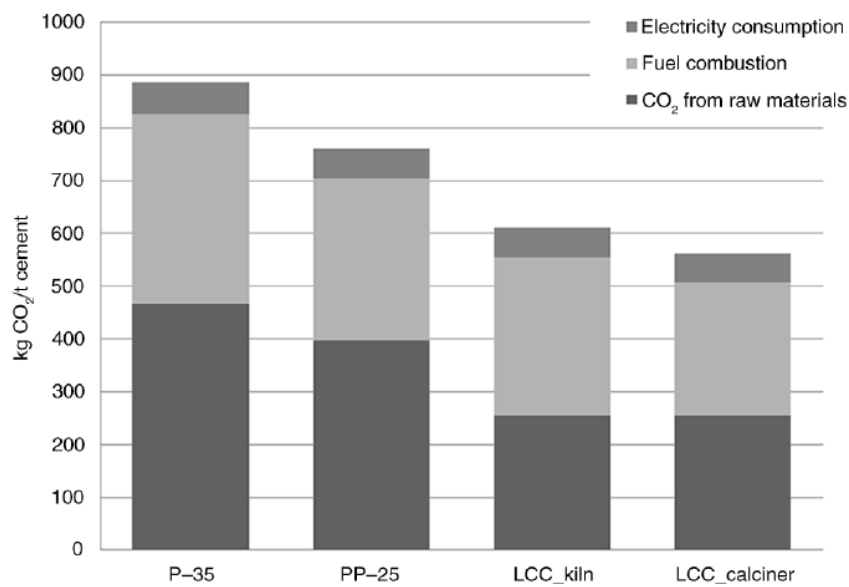
At industrial scale, in terms of environmental, social and economic impact, questions such as: “*Will different processing of metakaolin vary its environmental impact and therefore the overall environmental load of the blended cement?*” have been raised among researchers. In order to answer this and other questions, a careful analysis of the carbon footprint of the calcination of clays should be performed. The importance of calculating the environmental impact of concrete binder made of cement, limestone and metakaolin would allow us to understand their position in reference to the conventional concrete made of portland cement and commercially available Pozzolan-Portland-Cement (PPC) concretes. In order to evaluate their environmental performance, a formal Life-Cycle Assessment (LCA) of concrete with metakaolin needs to be completed and, a Life-Cycle Inventory (LCI) of each of its components should be developed.

LCA framework in buildings and in the construction sector in general has been used and widely accepted since 1990 [39]. The LCA method evaluates the environmental load of a product or a system throughout its entire life-cycle. This method accounts for all inputs and outputs relevant to the product processing and its methodology is standardized under ISO 14040:2006 [63]. This standard groups the process into 4 phases: Goal and Scope Definition, Inventory Analysis, Impact Assessment and Interpretation. In this section, a synthesis of existing literature on LCA studies that include metakaolin and cement blends using metakaolin and limestone is done in order to evaluate their scope and limitations and to highlight the main benefits of calcined clay limestone cements and their reduction of concrete’s greenhouse gas emissions.

Firstly, it is important to identify the environmental value of implementing metakaolin (MK) as a partial replacement of cement in the production of concrete. Current emission factors of MK are estimates based on approximations from cement’s manufacturing processes. Mikhailenko et al. [64] reported emissions of 175 kg CO<sub>2</sub>/tonne-MK from extraction of the raw material and fuel-derived emissions. This value was previously stated by Cassagnabere et al. in [65, 66] based on values reported by Gartner [8]. Unfortunately, details of calculations of this value are not mentioned in the latter paper. Moreover, Cassagnabere reports this emission factor later on in [67] and states that this value is supported on confidential data based on an environmental impact assessment.

Efforts to calculate the carbon footprint of concrete made with partial replacement of cement with MK have also been done by the Limestone-Calcined-Clay Cement (LC<sup>3</sup>) group based in Switzerland and led by Dr. Karen Scrivener (<https://www.lc3.ch/>) in close collaboration with the Cement Industry and researchers in Cuba and India. An industrial trial (pilot scenario) of LC<sup>3</sup> production in Cuba has been detailed by Vizcaino et al. [34]. During this industrial trial, a life-cycle assessment was conducted by the researchers and accounted for emissions caused by raw materials extraction and transportation, chemical decomposition of raw materials calcination, fuel (Cuban crude oil) emissions from thermal energy for the firing process and electricity consumption from cement grinding. Other processes were considered negligible and thus not included in the

analysis. Reduction in emissions were estimated to be approximately 270 kg CO<sub>2</sub>/tonnes (31% reduction), compared to Cuban PC and 125 kg CO<sub>2</sub>/tonnes, compared to traditional Cuban blended cement (20% zeolite and 5% gypsum). Because the emissions were estimated considering the calcination of MK to be conducted using a decommissioned wet rotary kiln, the emissions savings correspond to a scenario of low-efficient calcination process. Long-term solutions, including the retrofit of the outdated kilns to operate in dry conditions and/or the investment in new technology for flash calcination, would lead to greater savings in CO<sub>2</sub> emissions, thus, reducing the environmental burden of cement production in this region (Figure 2.6). The environmental efficiency of this blend was also assessed at large scale with the construction of a small house built with the ternary cement blend. Results showed that when the house was built using mortar and concrete blocks produced with this ternary blend, reductions of up to 30% in CO<sub>2</sub> emissions were achieved [41].



**Figure 2.6** - CO<sub>2</sub> emissions from cement production. P-35 corresponds to Cuban PC, PP-25 corresponds to traditionally produced Cuban blended cement and LCC corresponds to the ternary cement (limestone-calcined clay). Two scenarios of LCC production are considered (i.e., using an existing wet rotary kiln and implementing an industrial retrofitted calciner for dry process). Figure from Sanchez et al. [34]

Based on the previous work, a detailed life-cycle assessment study has been carried out by Sanchez et al. [39] on a cradle-to-gate basis in Cuba for three possible scenarios of application of MK in concrete: pilot production, foreseeable production scheme, and best available technology scenario. Table 2.3 shows input data for technology considered in each scenario and travel distances of the raw material to the cement factory.

**Table 2.3** - Input data for the Cuban Cement Industry according to different scenarios using calcined clay as partial replacement in cement. After Sanchez, et al. [39] Table 3.

| Indicators                   | Pilot level     | Industrial level                  | BAT level                         |
|------------------------------|-----------------|-----------------------------------|-----------------------------------|
| Kaolinite clay distance (km) | 150             | 60-150                            | <100                              |
| Type of fuel                 | Cuban crude oil | Pet-coke + Cuban crude oil        | Gas + waste                       |
| Clinker technology           | Wet rotary kiln | 4 stage pre-heater + pre-calciner | 6 stage pre-heater + pre-calciner |
| Clay calcining technology    | Wet rotary kiln | Retrofitted calciner              | Optimized flash calciner          |

For this study, emission factors; heating values of fuels; processes linked with extraction of raw materials and fuels; transportation; and electricity were taken from the Ecoinvent database and adapted to Cuban conditions. Additionally, consumption indexes; distances to raw materials sources; technology type; transportation modes; and extraction processes were also obtained from a collaboration with the Cuban Cement Industry and the Cuban Geological Survey. Finally, data to model the pilot scenario were based directly on the first industrial trial in Cuba reported by Vizcaino et al. [34]. In addition, these authors refer to values of energy from calcination of clay of 3235 MJ/t in a retrofitted kiln and 2775 MJ/t for clay calcined in a flash calciner. The data are disclosed as personal communications with FLSmidth & Co. It is unclear if these values of energy were used to calculate the contribution from clays' calcination to the overall environmental assessment of LC<sup>3</sup> cements. In all three scenarios, LC<sup>3</sup> cements show the lowest environmental impact in Cuba. Nevertheless, there are some discrepancies between these two studies. The consumption indices reported for energy consumption during clinker production and clay calcination do not match the values reported for the "Pilot Trial" studied by Sanchez et al. [39]. Furthermore, when multiplied by the emission factors proposed for this pilot trial, the CO<sub>2</sub> emissions (kg CO<sub>2</sub>/t) calculated do not appear to match accordingly. For instance, according to Vizcaino et al., 104.50 kg of crude oil are required for calcination of clay in a wet rotary kiln. This amount of crude oil is responsible for 342.76 kg CO<sub>2</sub>/t (emissions factor of 3.28 kg CO<sub>2</sub>/kg crude oil) and it is 33 times higher than the value of 31 kg of crude oil reported later by Sanchez et al. for the same process and under the same scenario of pilot trial with a wet rotary kiln.

A study made by Yu et al. [47] of the cradle-to-gate carbon emissions and embodied energy of cement blends that comprised portland cement and a blend of calcined clay and limestone in a 2:1 ratio (i.e., LC<sup>2</sup>) was performed and compared to those of cements made with 100% PC and cement blends made with fly ash at replacement dosages of 25-80% by weight. For each replacement ratio studied, values of embodied energy and CO<sub>2</sub> emissions were lower for cement blends containing fly ash than those containing LC<sup>2</sup> (15.1-66.6% less embodied energy and 6.8-45.7% less carbon emission for 25-80% total replacement levels). Since fly ash does not have to be thermally treated in order to render this pozzolan active, the embodied energy of cement blends containing high dosages of fly ash would naturally be lower than those with the same content of replacement by calcined clay. In addition, fly ash is a by-product of coal-fired electricity generation

and is considered to have little to no allocation on the carbon emissions of the production of these cement blends. Nevertheless, high dosages of fly ash in cement blends significantly reduce the heat of hydration of fresh concrete, hence delaying the strength gain at early ages [68]. In addition, fly ash availability is very limited and does not satisfy the demand for SCMs needed worldwide to reduce cement's carbon footprint in a significant matter [69]. Compared to PC, higher percentages of replacement with either LC<sup>2</sup> or fly ash reduced both the embodied energy and carbon footprint of cement when these metrics were compared by unit mass of cement. Furthermore, the authors quantified the environmental impact of each blend per unit of compressive strength of standard mortar cubes made with each blend and tested at different ages. In the study, three indexes were identified, the embodied energy index (EI) and the carbon emission index (CI), and the material cost index (COST). Interestingly, the LC<sup>2</sup> group had lower environmental impact and cost per 28-day unit strength (i.e., lower values of CI and COST indices), especially the LC<sup>2</sup> blend that considered 50% of total replacement. At higher dosages of replacement (i.e., above 60%) the EI index was determined to be lower. Higher dosages of clinker replacement significantly reduced the CH availability to promote the pozzolanic reaction of metakaolin. In terms of the environmental impact assessment, it is worth pointing out that the authors did not utilize inventory data of emissions from the region where they were modeling the cement blends and mortar. Materials were procured from different regions in the world and only production data was taken into consideration. Electricity grids and material compositions vary with the geographical location which renders each life-cycle analysis unique to the local context of the study. A complete approach would also account for upstream emissions beyond direct production of blended cements. In addition, when comparing both the embodied energy and the carbon emissions of all of the blends with their compressive strength at different ages, the comparison includes energy and emissions values by unit mass of cement and does not include the total volume and auxiliary materials involved in the process of producing mortar cubes for standard testing. This is important to consider given the differences in raw material content and w/b ratios considered for each blend which in turn plays an important role in the mechanical performance of the final specimen.

Specific data on life-cycle inventory emissions for calcined clay needs to be fully assessed. Heath et al. [70] reported a value of 423 g CO<sub>2-eq</sub>/kg of metakaolin based on the assumption that 1.16 kg of kaolin are required to obtain 1 kg of metakaolin after calcination. In addition, calculations of this figure were based on energy consumption of 2.5 MJ/kg of metakaolin using natural gas as fuel for clay calcination as determined for a feasibility study done by NLK Consultants in Canada [71]. Similar values have been published by other authors such as Jones et al. [72] whose cradle-to-gate analysis reported a value of 330 g CO<sub>2-eq</sub>/kg of metakaolin based on 400 kWh/t of embodied energy based on private communication with materials suppliers. Habert et al. [23] emphasizes the high variability of MK's embodied energy due to the type of fuel used during its calcination process. Reduced values of Global Warming Potential (GWP) of MK could be achieved when alternative heat sources (e.g., biomass heat) are used. These authors reported a value of 92.4 g CO<sub>2-eq</sub>/kg of MK when using low fuel values from biogas (agricultural waste) which is approximately 5 times lower than values reported above. Gettu et al. [73] proposed a value of 2.6 MJ/kg of clay required for its calcination based on estimates made by experts from the cement industry and calculations of specific heat and calcination energy from thermogravimetric analysis of several samples of clay. For their study, a life-cycle assessment was performed in order to compare the environmental profile of over 30 mix proportions of various concretes considering typical values from the Indian context.

The aforementioned researchers have pointed out that the use of metakaolin as a supplementary cementitious material has a bigger impact in cement’s environmental profile than the use of typically known waste materials such as fly ash and slag. As described in previous sections, in order to activate these clays, energy from fuel combustion during calcination is required in order to produce the reactive metakaolin. However, even though metakaolin’s production requires energy input for its calcination, its widely and ready availability is what makes this material a great potential substitute for other commercially available SCMs (e.g., fly ash, slag). Additionally, the majority of LCAs of blended cements using fly ash or slag do not include impacts associated with the processing of these materials into their analysis due to the consideration that these are waste products of the energy and steel industry. Nevertheless, a recent study by Habert et al. [23] points out that slag and fly ash are considered by-products of these industrial plants and therefore an environmental burden should be allocated to them. This environmental load should be applied based on an economic basis where the economic value of these by-products represents their share in the overall revenue of electricity and steel production. When these impacts are taken into account, the total environmental influence of concretes made with these SCMs could increase and even supersede that originated by cements blended with metakaolin.

LCA impact categories other than GWP during MK production have only been reported by Heath et al. [70] (See Table 2.4) based on the CML 2 (2002) baseline method [74] that was previously reported by Thurlow [75] with natural gas as the main heating source. Unfortunately, the latter reference is no longer available for review. A summary of emission factors and embodied energy per unit of mass of metakaolin found in recent peer-reviewed literature is shown in Table 2.5.

**Table 2.4** - CML2 baseline method impacts per kg of metakaolin. After [70, 75]

| <b>Impact category</b>          | <b>Unit</b>                      | <b>Metakaolin (kg)</b> |
|---------------------------------|----------------------------------|------------------------|
| Abiotic depletion               | kg Sb eq                         | 3.39E-03               |
| Acidification                   | kg SO <sub>2</sub> eq            | 1.03E-03               |
| Eutrophication                  | kg PO <sub>4</sub> eq            | 6.47E-05               |
| GWP (100 year)                  | kg CO <sub>2</sub> eq            | 0.421                  |
| Ozone later depletion           | kg CFC-11 eq                     | 3.98E-08               |
| Human toxicity                  | kg 1,4-DB eq                     | 0.0694                 |
| Fresh water aquatic ecotoxicity | kg 1,4-DB eq                     | 7.21E-03               |
| Marine aquatic ecotoxicity      | kg 1,4-DB eq                     | 32.4                   |
| Terrestrial ecotoxicity         | kg 1,4-DB eq                     | 8.66E-04               |
| Photochemical oxidation         | kg C <sub>2</sub> H <sub>4</sub> | 5.20E-05               |



**Table 2.5** - Summary of embodied energy and emission factors of metakaolin reported in recent literature.

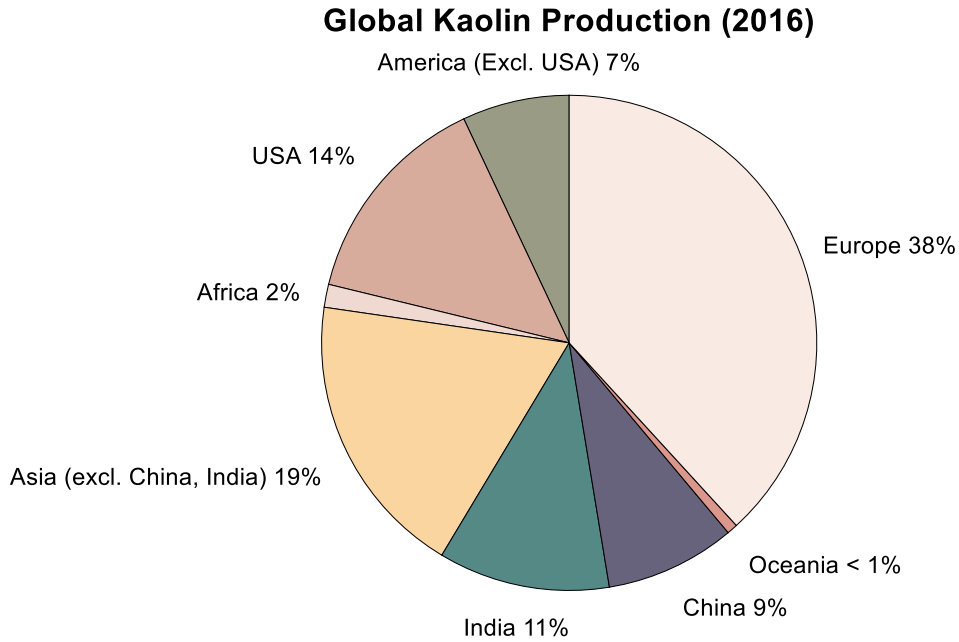
| Reference              | Embodied energy (MJ/t-MK) | Emission factor (kg CO <sub>2</sub> /t-MK) | Phases studied                           |
|------------------------|---------------------------|--|--|
| Gettu et al. (2018)    | 2600                      | *  | Extraction / processing / transportation |
| Habert (2016)          | 4100                      | 92.4                                       | Processing / transportation              |
| Heath et al. (2014)    | 2500                      | 423  | Extraction / processing                  |
| Jones, et al. (2011)   | 1429                      | 330  | Extraction / processing                  |
| Mikailenko (2012)      | *                         | 175  | Extraction / processing                  |
| NLK (2002)             | 2500                      | 370  | Extraction / processing                  |
| Sanchez et al. (2016)  | 3235                      | *  | Extraction / processing / transportation |
| Thurlow (2005)         | *                         | 421  | Unknown                                  |
| Vizcaino et al. (2015) | *                         | 342.76                                     | Processing only                          |

It is worth noting that there is still a lack of rigorous data in literature for the environmental impact of metakaolin and its use as SCMs in cement and concrete production, thus, Chapter 4 describes a life-cycle inventory framework to calculate the life-cycle environmental impacts of metakaolin production which in turn will allow for a complete assessment of the environmental burden of concretes made with blends of OPC, MK, and limestone.

As previously mentioned, the use of SCMs as partial replacement of cement has proven to provide comparable mechanical performance as ordinary portland cement. However, cost and lack of widespread availability of currently used sources of SMCs (e.g., fly ash and slag), are key factors in determining the extent to which they could be used in the future. Calcined clays seem to be an effective solution to overcome the lack of quantities needed to render SCMs a robust mitigation strategy for the cement industry. Especially if planning to meet the targeted emissions reduction set by 2050 [11]. Figure 2.7 shows the most recent data on world production of kaolin by region and main countries during 2016. Data was obtained from the 2016 Minerals Yearbook report for clay and shale [76]. Approximately, 37.5 million metric tonnes of kaolin are produced worldwide from which 14.2% (5.3 million tonnes) were produced solely in the United States. This figure is almost equal to the total amount of kaolin produced in Asia (excluding China and India) and it was only surpassed by production in Europe for that year (14.3 million tonnes). However, US levels of production during this year were less than a half of the total production of this mineral across Europe. India is also a main producer of kaolin, accounting for 11.2% of the global production (4.2 million tonnes). The availability of this clay mineral has brought the attention of cement industry to explore its application as alternative SCMs at industrial scale.

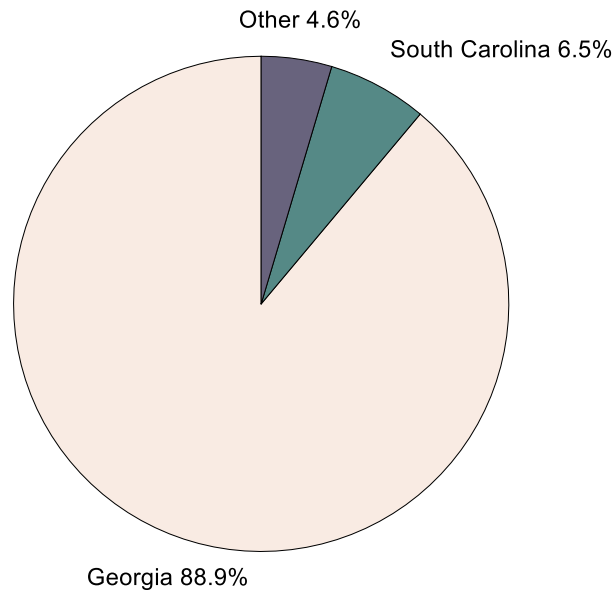
Kaolin in 2016 was sold in the US as airfloat, calcined, delaminated, unprocessed and water-washed. Due to kaolin's various properties, the market share of the production of this mineral covers a very wide range of applications including ceramics, refractories, fillers,

extenders, binders, and heavy-clay products such as bricks and portland cement. Portland cement accounted for 2% of the total production of kaolin in 2016. Figure 2.8 presents the national distribution of kaolin production by state. Georgia is the leading producer of kaolin in the country, with 89% of the market, whereas only 5% of kaolin sold in 2016 was produced in secondary states such as Alabama, Arkansas, California, Florida, Nevada, and Texas.



**Figure 2.7** – 2016 kaolin world production by region and main countries. Data from USGS Minerals Yearbook—2016 [76]

### Kaolin sold or used by producers in the U.S. (2016) by state



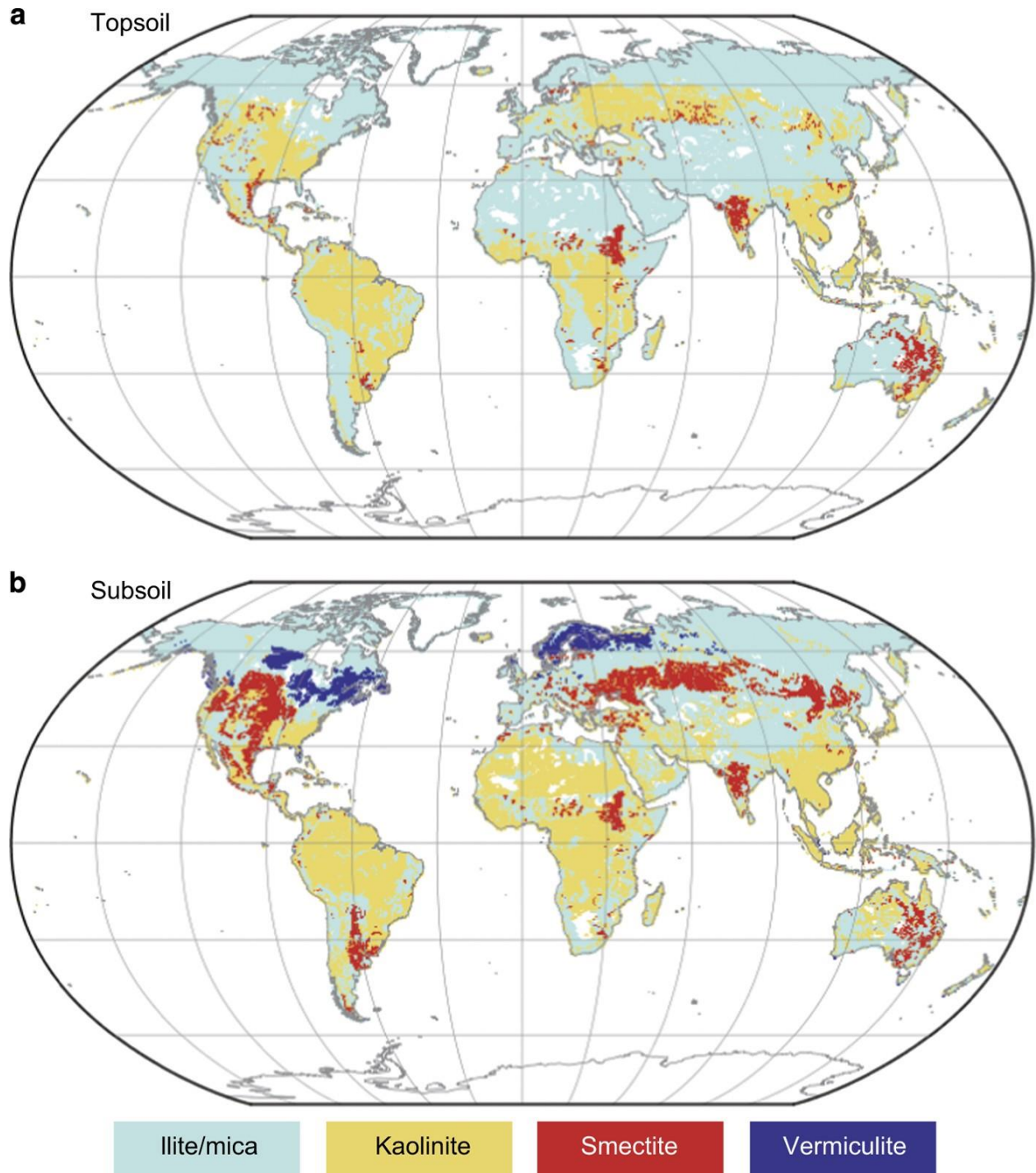
**Figure 2.8** - Kaolin sold in the US in 2016 by state. Percentages based on total amount of 5,312 thousand metric tonnes. “Other” includes: Alabama, Arkansas, California, Florida, Nevada, North Carolina, and Texas. Data from USGS Minerals Yearbook—2016 [76]

It is worth noting that these data are only accounting for clays with high purity (i.e., more than 90% content of kaolinite mineral). Even though high-grade kaolin’s main industrial use is focused in the production of paper products, ceramics and chemicals, it has been proven that medium- and low-grade kaolin clays, which are not used in these industries, could also compete with the strength requirements of PC when unburned limestone is added to the cement blend [34, 41]. However, estimates of availability for medium- and low-grade kaolinitic clays has not been extensively assessed since it has very little or no commercial use. Detailed analysis of production of clay minerals with medium- and low-grade content of kaolin by region and within countries should be assessed in order to make a more accurate estimation of the effective availability of suitable kaolinite clays and identify the location of these deposits and potential production sites. With this information, a complete mapping of suitable raw materials could be done to estimate the sustainability value of calcined clays in cement, accounting for transportation emissions with real data of transportation distances between the optimal locations of deposits, production sites, and cement or concrete manufacturing facilities.

Alujas et al. [77] discussed a methodology for the preliminary evaluation of the Cuban clay deposits. The methodology highlights the benefits of identifying and classifying those clay deposits that contain lower purity kaolinite. As shown previously, official data on kaolin clay availability is subject to its commercial and industrial use. Estimation of the reserves of these clays are assessed following the rigorous criteria for kaolinite clay used in the ceramics and paper industry, where clays with lighter colors (especially white) are exclusively desired for these industries. The authors proposed a methodological investigation that comprised different

parameters related to the chemical content of the group of minerals with kaolin content in potential clay samples. These parameters were based on previous work [55, 78] which identified that the most reactive clays (i.e., those with the highest pozzolanic activity) contained 40% or more kaolinite mineral. Based on this criterion, the chemical composition of clay to be considered adequate was established as:  $\text{Al}_2\text{O}_3 \geq 18\%$ ,  $\text{Al}_2\text{O}_3/\text{SiO}_2 \geq 0.30$ , and “loss on ignition” (LOI)  $\geq 7\%$ . With these criteria, the authors were able to classify different clay samples obtained from different deposits in Cuba and run a preliminary assessment of their feasibility as SCMs in blended cement. This assessment is a good guidance when trying to screen for good sources of kaolin clays suitable for cement and concrete applications. In addition, it allows to complement the selection of appropriate clays when TGA test results are skewed due to the presence of impurities or other clay minerals that contribute to the weight loss in the temperature range identified as characteristic for kaolin dehydroxylation. Hence, rendering difficult to separate each contribution from the total weight loss reported in the test results which can cause overestimation of the content of kaolinite mineral in the clay sample.

Researchers in other fields of study have developed global datasets to model clay-size mineral maps at a global scale [79-81]. Even though their work focuses on applications such as integrated studies on biogeochemistry, climatology, estimation of global dust emission, and other earth sciences, mapping of clay soils could help in visualizing the principal regions in the world rich in soils containing the mineral group of kaolinite clay that could potentially be explored as SCM in cement production. Recent dataset developed by Ito and Wagai [82] show data of soil clay discretized by its mineral composition with respect to the ten main clay-size mineral groups (i.e., Gibbsite, Kaolinite, Illite/mica, Smectite, Vermiculite, Chlorite, Iron oxide, Quartz, Non-crystalline, and others) for both topsoil and subsoil in arid and humid lands. Figure 2.9 shows the global distribution of the most abundant clay mineral groups. It is worth noting that kaolinite soils are especially abundant in those regions where the majority of emerging countries are located (e.g., South America, Africa, South Asia), emphasizing the potential for a robust SCM that could be used in regions where other mitigation technologies to reduce cement’s environmental impact in the immediate future are still out of reach.



**Figure 2.9** – Global distribution of the most abundant clay groups in both topsoil and subsoil. Figure developed by Ito and Wagai in [82].

Careful work on clay deposits’ assessment and the life-cycle assessment of this materials as SCMs in cement blends at industrial scale have only been limited to specific conditions in Cuba and India. A global assessment of their impact in relation with the potential reduction on GHG emissions associated with the use of conventional PC concrete mixtures would allow their

optimum application in building construction and infrastructure to be identified. Given its exceptional characteristics, lower calcination temperature than that of PC for complete activation, good interaction with limestone in cement blends, and durability performance, calcined kaolinite clays (i.e., metakaolin) are considered now a great mitigation strategy to reduce the environmental burden of cement production in the short and medium term.

Ultimately, the manufacturing maturity of cements with portland cement clinker, metakaolin, and limestone is still incipient and requires the adoption or retrofit of dedicated kilns to conduct the calcination of the raw clays. Sanchez et.al in [39] showed a comparison of the operational costs of traditional portland cement and limestone, calcined clay cements (LC<sup>3</sup>) in Cuba. The operational cost of portland cement was \$55 USD/tonne of cement approximately, whereas LC<sup>3</sup> cements were estimated to have operational costs of approximately \$50 USD/tonne of cement (10% reduction). Other economic feasibility scenarios of LC<sup>3</sup> production are reported by Scrivener et. al in [83] in which clay calcination was assessed in scenarios using either a flash calciner or a rotary kiln based on average values from emerging countries. In addition, distance of the raw suitable clay was also considered as far from the plant (i.e., 200 km) and close to the plant (i.e., 10 km) and considered coal as the main fuel source for production. Estimated production costs varied from \$23.4–\$36 USD/tonne of LC<sup>3</sup> cement produced with a flash calciner to \$24.2–\$36.5 USD/tonne produced with a rotary kiln. The scenarios were compared with the benchmark cost of production of PC type I (i.e., \$30 USD/tonne of cement produced in a plant or \$47 USD/tonne of cement if produced with imported clinker which emphasizes the lower cost of LC<sup>3</sup> cements.

# Chapter 3 – Investigation of the Clay to Limestone Ratio on the Hydration of Cement Blends

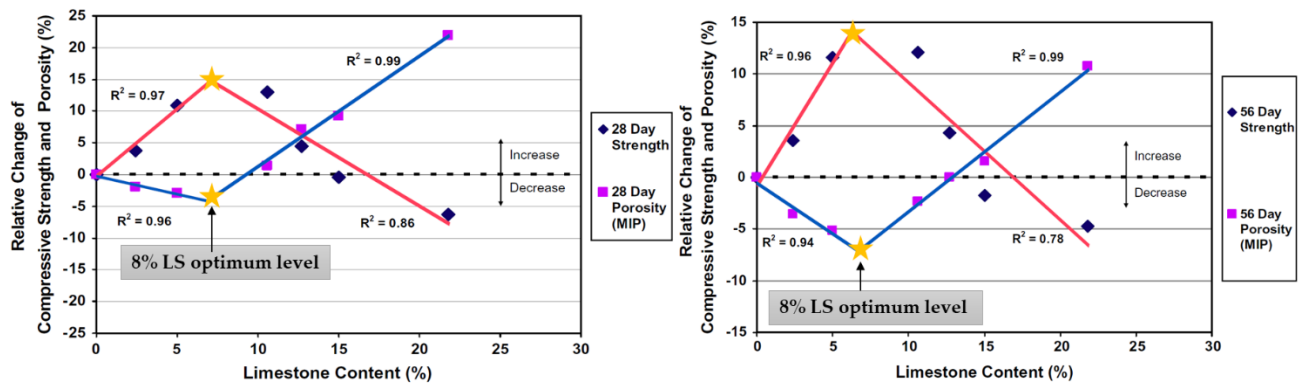
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## 3.1 Background

The overwhelming demand for cement-based materials to satisfy the rapid expansion of the built environment worldwide is a cause of concern regarding these materials' environmental impact. In light of this, the cement industry has adopted global goals and mitigations strategies to reduce the impacts of cement and concrete production in the climate change. In order to mitigate these emissions, the 2009 and 2018 Technology Roadmap reports developed by the World Business Council for Sustainable Development (WBCSD) and the International Energy Agency (IEA) for the low-carbon transition in the cement industry highlighted the capture and storage of CO<sub>2</sub> (CCS) as the most important strategy to achieve the reduction goals in accordance to the 2°C scenario targets for 2050 which aims to limit the rise in global temperatures to less than 2°C above pre-industrial levels by 2100 [11]. Although extensive research has been undertaken on CCS, these technologies are still highly expensive and lower cost solutions are required for emerging countries where the vast majority of the cement demand will be located in the next 50 years [25]. Furthermore, The United Nations Environmental Program - Sustainable Building and Climate Initiative (UNEP-SBCI) published a report in 2016 titled “Eco-efficient cements: Potential economically viable solutions for low-CO<sub>2</sub> cement-bases materials industry” in which several readily implementable and less expensive solutions for CO<sub>2</sub> mitigation in the cement and concrete value chain could significantly improve the reduction scenario proposed by the previous roadmaps [15]. The UNEP-SBCI working group stressed the importance of expanding the use of supplementary cementitious materials (SCMs) and thus, reducing the clinker-to-cement ratio as a way to transition to more sustainable low-carbon cement-based materials. The current benchmark of clinker-to-cement ratio of 0.65-0.75 is widely accepted globally [16]. However, these ratios are not considering potentially more widely available SCMs such as calcined clay which coupled with limestone has proven to achieve similar mechanical properties than those of plain portland cement materials with a clinker substitution of up to 50% [84]. The reduction of clinker content in cement-based materials as a CO<sub>2</sub> mitigation strategy for wide use especially in developing countries, inspired the experimental plan described herein. This chapter was developed to study the effect of increased reduction in the clinker-to-cement ratio (i.e., up to 0.45) with the use of a coupled substitution of cement with calcined clay and limestone in order to understand their effect in the mechanical and durability properties of mortars and concretes made with different total replacement ratios of these materials.

The use of limestone (LS) coupled with SCMs in portland cement blends has been widely accepted due to similar hydration products obtained from those of cement's hydration using 100% portland cement (PC). However, the stoichiometry and hydration rate of these products differ slightly due to the influence of the alternative constituents [85], therefore affecting the performance of the hardened pastes. Previous studies on physico-chemical properties of cement blends made with replacement of portland cement with metakaolin (MK) have found an increased initial setting time, high compressive strength values at early ages, and an improvement in mechanical and durability performance [86]. A reduction in workability due to metakaolin's high surface area has been observed [45, 84, 87]. Yet, the use of water-reducing admixtures such as

superplasticizers (e.g., polycarboxylate ether based or PCE) have shown to improve the workability of mixtures containing metakaolin. The dosage of superplasticizer could vary from 0.01% to 1% by weight of binder depending on several factors including the purity of the metakaolin [36, 45]. Additionally, packing optimization in concrete has been used to improve the workability [88-90]. The enhancement of the early age properties is often attributable to MK acting as a filler and accelerating the hydration of cement phases. When combined with raw limestone, other hydration products are observed, such as carboaluminate hydrates (i.e., hemicarboaluminates<sup>3</sup> and monocarboaluminates<sup>4</sup>) [34, 42]. These hydration products contribute to strength development due to their effect on pore structure enhancement [85]. At later ages, the increase in strength is highly due to the pozzolanic reaction between the MK and the portlandite (i.e., calcium hydroxide or CH) produced during cement hydration. Ramezaniapour and Hooton [85] studied the effect of limestone content in blends of 90% cement and 10% metakaolin, and concluded that 8% of LS is the optimum level for these blends in order to obtain the highest relative compressive strength at the lowest porosity. For their study, cements containing different levels of LS were mixed with 10% MK and compressive strengths and porosities were measured at 28 and 56 days. Their results are observed in Figure 3.1.



**Figure 3.1** - Relative strength and porosity of mortar cubes made with 90% cement and 10% MK indicating the optimum level of LS at 8%. Left: 28-day compressive strength. Right: 56-day compressive strength. Red lines represent the relative strength and blue lines represent relative porosity. Adapted from [85].

This behavior of cement pastes with MK and LS was also validated by Alujas et al. [91]. It seems to be clear that the effect of calcined clays in blended systems is a combination of filler effect during the first stage of hydration and an increased mechanical performance due to the pozzolanic effect at later ages. In addition, these authors confirmed that clays with moderate contents of kaolinite mineral are a great source of highly reactive SCMs.

Pore refinement phenomenon of blends with metakaolin and limestone has also been confirmed by Antoni et al. [42] for blended systems with a combination of portland cement, metakaolin and limestone with a metakaolin to limestone ratio of 2:1 and various replacement levels studied through mercury intrusion porosimetry. The effect of decreased pore size and distribution has a positive impact in the concrete's resistance to chloride penetration as studied by Shi et al. [53] and Pierkes et al. [92]. The former compared the chloride penetration after 28 days

<sup>3</sup>  $3\text{CaO}-\text{Al}_2\text{O}_3-0.5\text{Ca}(\text{OH})_2-0.5\text{CaCO}_3-11.5\text{H}_2\text{O}$

<sup>4</sup>  $3\text{CaO}-\text{Al}_2\text{O}_3-\text{CaCO}_3-11\text{H}_2\text{O}$



of hydration of mortars with 35% replacement of cement with metakaolin and limestone (3:1 ratio), and that of a reference mix with 100% of portland cement. Results showed a reduction in the chloride penetration depth of the samples. Similar behavior was confirmed by Pierkes' work. Besides the positive effect of pore refinement in systems containing metakaolin and limestone, Dhandapani et al. [45] stated that more reactive aluminate ions coming from the metakaolin dissolution lead to the binding of chloride ions which hinders their further intrusion in the system. Results from total charge passed in the chloride penetration resistance test according to the ASTM C1202 standard of LC3 blends (50% PC, 35% metakaolin, 15% limestone, and 5% gypsum) showed a minimal amount of charge passed (i.e., category *low* as per ASTM C1202 classification) which indicates their potential excellent resistance against corrosion.

The following sections describe the experiments conducted on mortar and concrete samples containing coupled substitutions of calcined clay and limestone. The objective of the experimental plan is to understand the effects of the variation of clay-to-limestone ratio on compressive strength and chloride penetration resistance of mortars and concrete made with ternary blends of cement, metakaolin, and limestone. In addition, the influence of different clay sources with varying calcined kaolinite content and varying limestone replacement ratios in these properties is also explored. As the cement industry transitions to more sustainable low-carbon cements, there is a need to further understand what the differences between “high grade” and “low grade” metakaolin are and their effects in cement and concrete mixes in terms of replacement levels, mechanical performance, durability, environmental and economic impact. As a note, in this chapter the terms calcined clay and metakaolin are used interchangeably and both correspond to reactive, amorphous clay with kaolinite mineral content.

## **3.2 Materials**

### **3.2.1 Portland cement and Limestone Additions**

ASTM portland cement Type II/V was used for both mortar cubes and concrete cylinders. Table 3.1 shows the composition of portland cement used in all of the mixtures studied. All specimens were cast using different combinations of metakaolin (MK) and limestone (LS) with PC. In order to explore the effect of varying clay-to-limestone ratios, 5%, 10%, 15% and 20% of cement were replaced with LS and a coupled constant substitution of 35% of cement with MK. The composition of the different systems is summarized in Table 3.2. The limestone used was Betocarb F – LU, from Omya Inc. and its composition is detailed in Table 3.1.

**Table 3.1** - Phase composition of cement and limestone measured by XRD.

| <b>Cement</b>     | <b>Content [%]</b> | <b>Cement</b> | <b>Content [%]</b> | <b>Limestone</b> | <b>Content [%]</b> |
|-------------------|--------------------|---------------|--------------------|------------------|--------------------|
| C <sub>3</sub> S  | 48.4               | Periclase     | 0.1                | Quartz           | 0.23               |
| C <sub>2</sub> S  | 26.4               | Quartz        | 0.4                | Calcite          | 99.77              |
| C <sub>3</sub> A  | 1.7                | Gypsum        | 1.0                |                  |                    |
| C <sub>4</sub> AF | 12.3               | Hemihydrate   | 2.3                |                  |                    |
| Free lime         | 0.2                | Anhydrite     | 0.3                |                  |                    |
| Portlandite       | 2.1                | Calcite       | 4.6                |                  |                    |
|                   |                    | Dolomite      | 0.2                |                  |                    |

**Table 3.2** - System composition of blends studied (% of total cementitious materials).

|         | <b>Cement [%]</b> | <b>Metakaolin [%]</b> | <b>Limestone [%]</b> |
|---------|-------------------|-----------------------|----------------------|
| Control | 100               | 0                     | 0                    |
| 35:05   | 60                | 35                    | 5                    |
| 35:10   | 55                | 35                    | 10                   |
| 35:15   | 50                | 35                    | 15                   |
| 35:20   | 45                | 35                    | 20                   |

### 3.2.2 Kaolinitic Clays

Three kaolinitic clays with varying compositions and origin were studied. Calcination of all the clays sourced was performed elsewhere. The designated codes of each calcined clay studied are as follows: K0 corresponds to metakaolin provided by BASF USA (MetaMax®), K1 and K2 correspond to calcined clays from Brazil commonly used in the ceramic industry. Characterization of K0, K1, and K2 is described herein. Quantification of phases measured by X-ray diffraction (XRD) - Rietveld method was only performed for K0 (Table 3.3). Unfortunately, the quantity of material supplied for K1 and K2 was very limited and only qualitative XRD tests were performed. Thermogravimetry analysis (TGA), particle size distribution, and the pozzolanic activity index of samples of K1 and K2 were elaborated by [93]. For all the calcined clays, the kaolinite content is indicated in Table 3.4.

**Table 3.3** - Phase composition of SCMs used in blends measured by XRD.

| <b>K0</b>           | <b>Content [%]</b> |
|---------------------|--------------------|
| Quartz              | 0.1                |
| Anastase            | 1.5                |
| Amorphous clay (MK) | 98.4               |

**Table 3.4** – Origin and calcined kaolinite content of clays studied.

| <b>Calcined Clay</b>           | <b>K0</b> | <b>K1</b> | <b>K2</b> |
|--------------------------------|-----------|-----------|-----------|
| Origin of clay                 | U.S.      | Brazil    | Brazil    |
| Calcined kaolinite content (%) | 98.4      | 82.0      | 43        |

To ensure workability of the mortar mixes, MasterGlenium 7920, a polycarboxylic ether (PCE) based superplasticizer provided by BASF USA was used. Table 3.5 shows the weight percentage (wt.%) of superplasticizer used in each of the blends studied. The weight percentage corresponds to the percentage by weight of total solids in the mix excluding sand.

**Table 3.5** – Superplasticizer content in weight percentage (wt.%) of total binder.

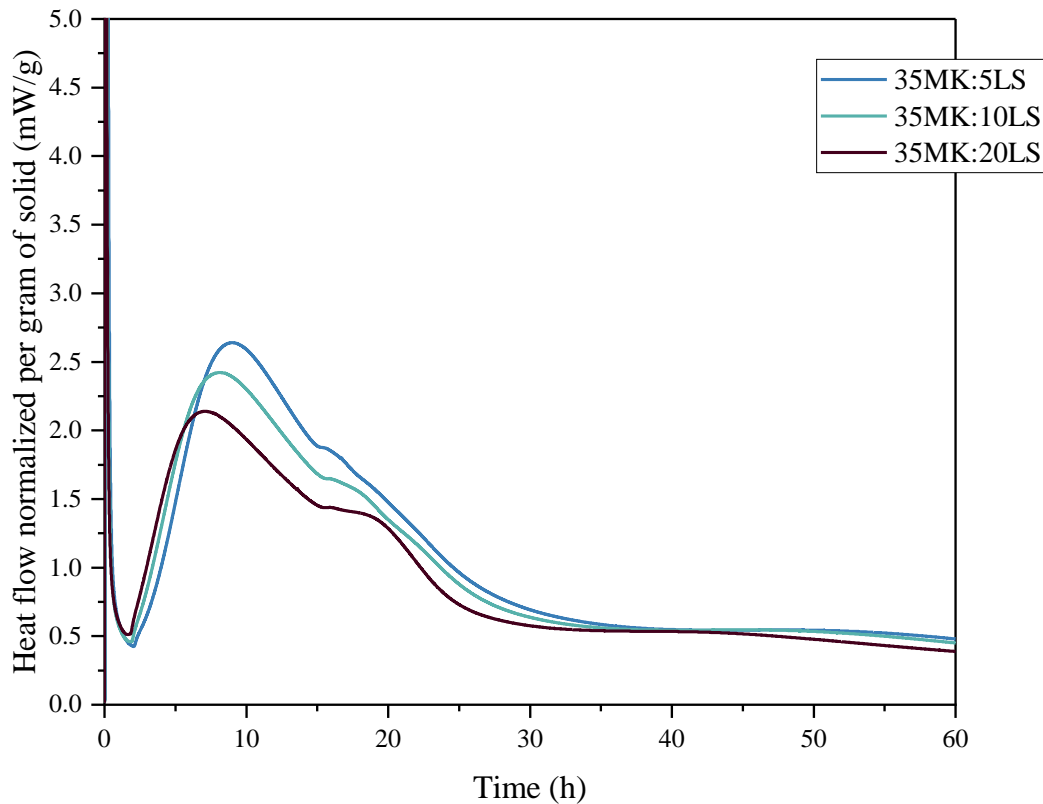
| <b>Calcined Clay</b> | <b>Metakaolin Content (%)</b> | <b>35:5</b> | <b>35:10</b> | <b>35:15</b> | <b>35:20</b> |
|----------------------|-------------------------------|-------------|--------------|--------------|--------------|
| K0                   | 98                            | 0.3         | 0.3          | 0.3          | 0.3          |
| K1                   | 82                            | N.A.        | N.A.         | 0.1          | 0.1          |
| K2                   | 43                            | 0.3         | 0.3          | 0.1          | 0.1          |

### 3.2.3 Sulfate Adjustment

Blended cements with high substitution levels of clinker with supplementary cementitious materials rich in aluminates (e.g., metakaolin) need to pay special attention to the potential effects of lower sulfate contents in the pastes [42, 45, 94, 95]. Previous research [42, 94-96] demonstrated that without a proper gypsum adjustment, the separation of silica and alumina peaks on heat flow curves from calorimetry results were not very well distinguished, therefore compromising the setting times of the mixes and the early strength development (i.e., the slowing down of the clinker hydration [95]). Gypsum adjustment is of importance in these set of mixes since the excess of aluminates coming from the metakaolin could potentially shift the peak of occurrence of silica from C<sub>3</sub>S hydration and the peak from the aluminates coming from the dissolution of C<sub>3</sub>A in cement and metakaolin. In portland cement hydration processes, when C<sub>3</sub>A dissolves in the solution, it reacts with the sulfates (e.g., gypsum) available to form ettringite. Ettringite is stable as long as sulfates are still available in the system and when it starts to form, the aluminum concentration in the solution decreases until the “sulfate depletion point” is achieved indicating

the maximum dissolution of aluminates and the peak of ettringite formation [96]. The sulfate depletion point occurs after the main peak of precipitation of the silicate hydrates from the  $C_3S$  reaction which represents the end of setting and the onset of hardening. This peak is crucial in cement hydration since the massive precipitation of C-S-H and CH control the setting and hardening onset of cement paste. When a second source of aluminates is incorporated in the system (e.g., metakaolin), the silicate-aluminate-sulfate balance is altered, and the sulfate depletion point occurs much faster than the silicate peak. In the absence of sulfates to react with the alumina in dissolution, a delay in the silicate hydration is observed. In addition, the use of superplasticizers to improve workability often delays the onset of the hydration peak. This phenomenon is still not fully understood, thus, a close monitoring of the effect of superplasticizer dosage in the hydration of these systems has to be done to guarantee the occurrence of the silica peak first and an acceptable delay in the onset of setting [97].

To prevent the system to be undersulfated, gypsum adjustment was achieved for the mixtures that contained metakaolin, by adding calcium sulfate dihydrate (3 wt.% of total binder) to each mixture. Gypsum optimization is important to ensure ettringite formation and dissolution of  $C_3S$ . Addition of gypsum is valid up to 5-6% in order to avoid sulfate expansion in hardened cement mortar [42, 98]. Isothermal calorimetry tests for the blends 35MK:5LS, 35MK:10LS, and 35MK:20LS with calcined clay K0 were conducted at ETH in Switzerland to study the heat evolution of the blends, the adequacy of the sulfate adjustment and the effect of superplasticizer addition during the onset of paste setting. Results shown in Figure 3.2 confirmed the effectiveness of the gypsum adjustment.



**Figure 3.2** - Influence of sulfate adjustment on the heat released by isothermal conduction calorimetry of mortar blends with constant water-to-binder ratio [w/b=0.45]. Mortar blends contained K0 calcined clay.

### 3.3 Mixture Proportioning

The experimental plan comprised the design and casting of several mortar and concrete mixes. Mortar mixes were built to fill in 50-mm (2-in) standard cubes for compressive strength testing. Mortar mixes had the same water-to-binder (w/b) ratio of 0.45 and 1 part of binder to 2.75 parts of graded standard silica sand by mass. The binder was composed of a mix of portland cement, metakaolin, and limestone at different dosages. Gypsum was optimized as detailed in Section 3.2.3. To studied concrete under compression and its resistance to chloride penetration (RCPT), all concrete mixes were designed as per ACI 211.1 containing a w/b ratio of 0.57 and a 28-day design compressive strength of 28 MPa (4000 psi). The coarse aggregate used for the concrete mixes consisted of pea gravel with maximum size of 10-mm (3/8-in) and the fine aggregate had a fineness index of 3.16. Mix designs are detailed in Table 3.6.

**Table 3.6** – Mix designs of different mortars and concretes considered in this study.

| Mixture set | Calcined clay I.D. | Mix I.D.  | w/b  | No. of samples <sup>1</sup> | Cement            | Calcined clay | Limestone | Gypsum | Water | Fine aggregate | Coarse aggregate | SP <sup>2</sup>      |
|-------------|--------------------|-----------|------|-----------------------------|-------------------|---------------|-----------|--------|-------|----------------|------------------|----------------------|
|             |                    |           |      |                             | kg/m <sup>3</sup> |               |           |        |       |                |                  | (% by wt. of binder) |
| Mortar      | N.A.               | Control   | 0.45 | 3                           | 554               | 0             | 0         | 0      | 249   | 1523           | 0                | 0.15                 |
|             | K0, K1, and K2     | 35MK:5LS  | 0.45 | 3                           | 339               | 188           | 10        | 17     | 249   | 1523           | 0                | 0.3                  |
|             |                    | 35MK:10LS | 0.45 | 3                           | 311               | 188           | 38        | 17     | 249   | 1523           | 0                | 0.3                  |
|             |                    | 35MK:15LS | 0.45 | 3                           | 283               | 188           | 66        | 17     | 249   | 1523           | 0                | 0.3                  |
|             |                    | 35MK:20LS | 0.45 | 3                           | 255               | 188           | 95        | 17     | 249   | 1523           | 0                | 0.3                  |
| Concrete    | N.A.               | Control   | 0.57 | 3                           | 401               | 0             | 0         | 0      | 228   | 934            | 700              | 0                    |
|             | K0                 | 35MK:5LS  | 0.57 | 3                           | 245               | 136           | 7         | 12     | 228   | 934            | 700              | 0.3                  |
|             |                    | 35MK:10LS | 0.57 | 3                           | 225               | 136           | 28        | 12     | 228   | 934            | 700              | 0.3                  |
|             |                    | 35MK:15LS | 0.57 | 3                           | 205               | 136           | 48        | 12     | 228   | 934            | 700              | 0.3                  |
|             |                    | 35MK:20LS | 0.57 | 3                           | 184               | 136           | 69        | 12     | 228   | 934            | 700              | 0.3                  |
|             | K1, K2             | 35MK:5LS  | 0.57 | 1*                          | 245               | 136           | 7         | 12     | 228   | 934            | 700              | 0.3                  |
|             |                    | 35MK:10LS | 0.57 | 1*                          | 225               | 136           | 28        | 12     | 228   | 934            | 700              | 0.3                  |
|             |                    | 35MK:15LS | 0.57 | 1*                          | 205               | 136           | 48        | 12     | 228   | 934            | 700              | 0.1                  |
|             |                    | 35MK:20LS | 0.57 | 1*                          | 184               | 136           | 69        | 12     | 228   | 934            | 700              | 0.1                  |

<sup>1</sup>Corresponds to the number of samples tested under compression at each testing age (i.e., 1, 3, 7, 28, 56, and 90 days). Samples made for RCPT tests followed the same concrete mix designs and mixing protocols.

<sup>2</sup>SP % denotes the amount of superplasticizer solids (SP content) as percentage of total mass of binder.

\*Due to limited material quantities, only one sample of each mix I.D. was tested at 56 days (2 samples of K1, and 4 samples of K2).

## **3.4 Test Methods**

### **3.4.1 Compressive Strength and Elastic Modulus**

For mortar strength tests, 50-mm (2-in) standard cubes were cast and tested following ASTM C109 [99]. The specimens were demolded after 24 hours and cured under saturated limewater until the desired curing times. Compressive strength evolution was assessed at 1, 3, 7, 28, 56, and 90 days for each mortar blend containing each of the clays under study (i.e., K0, K1, and K2). The average compressive strength for each mix was evaluated based on results from three samples of the same mortar composition at each test date.

For concrete strength tests, cylindrical specimens of 101.6-mm (4-in) diameter and 203.2-mm (8-in) of height were cast following ASTM C192 [100]. These specimens were also demolded after 24 hours and cured in a moisture-controlled room until the day of testing. Three samples per mix design containing K0 metakaolin were tested under compressions at 1, 3, 7, 28, 56, and 90 days. Only one specimen per each of the mix designs containing K2 was tested at 56 days. Only one sample for mixes 35MK:15LS and 35MK:20LS each containing K1 was tested at 56 days.

Static elastic modulus tests were performed on concrete cylinders of 150-mm (6-in) diameter and 300-mm (12-in) of height following ASTM C469 [101]. Only concrete cylinders of each mix design containing K0 metakaolin were tested at 28 days. Each specimen was loaded to 40% of the ultimate compressive strength ( $f'_c$ ) and unloaded completely during three separate cycles. The elastic modulus was determined as the slope of the third cycle from the stress-strain response of each specimen.

### **3.4.2 Chloride Penetration Resistance**

Chloride penetration resistance was assessed following ASTM C1202 [102] for which 100-mm by 200-mm (4-in by 8-in) concrete cylinders were cast. This test provides a qualitative measure of the concrete's resistance to chloride ingress [45]. For each concrete mixture, two cylinders were cast, demolded after 24 hours and cured in a moist room until the day of testing (a total of ten concrete cylinders). Sample preparation prior to the test involved saw-cutting two 50-mm (2-in.)-thick disks from each concrete cylinder, followed by saturation under water for 18 hours after specimens were subject to full vacuum for 4 hours. Test specimens were then mounted on a dual-cell system and each end was exposed to a sodium hydroxide (NaOH) solution and a sodium chloride (NaCl) solution respectively (3.0% NaCl and 0.3 N NaOH). Both ends of each cell were connected to a positive and negative terminal of the unit channel. The test measured the electrical current passing through each end of the saturated concrete disk for a period of 6 hours at a standard voltage of 60 V [103]. The total charge passed was calculated using the PROOVE<sup>®</sup>it software and equipment by German Instruments. The total charge passed gave an estimation of the concrete's resistance to chloride ingress as per ASTM C1202.

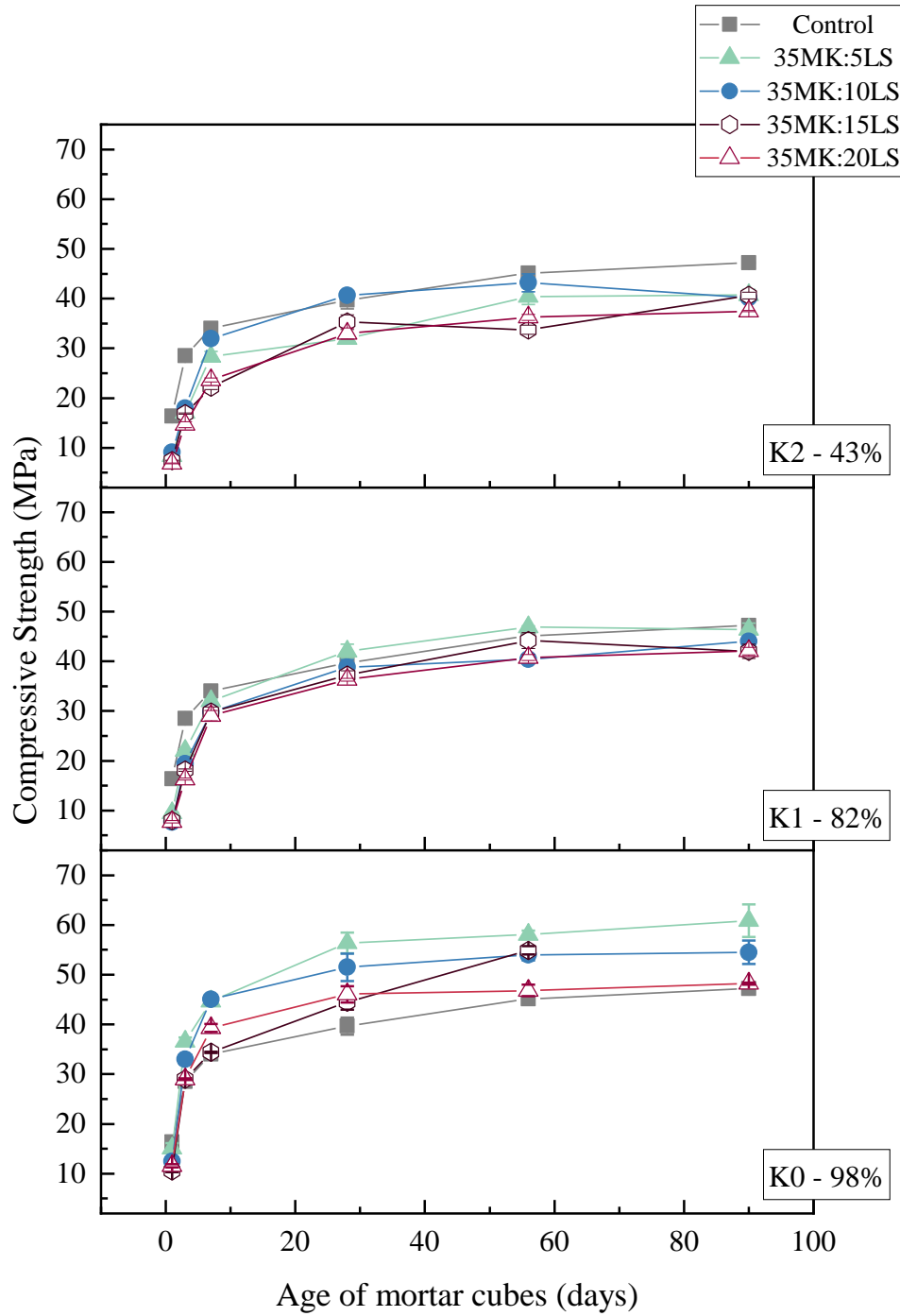
## 3.5 Results and Discussions

### 3.5.1 Mechanical Properties Under Compression Loading

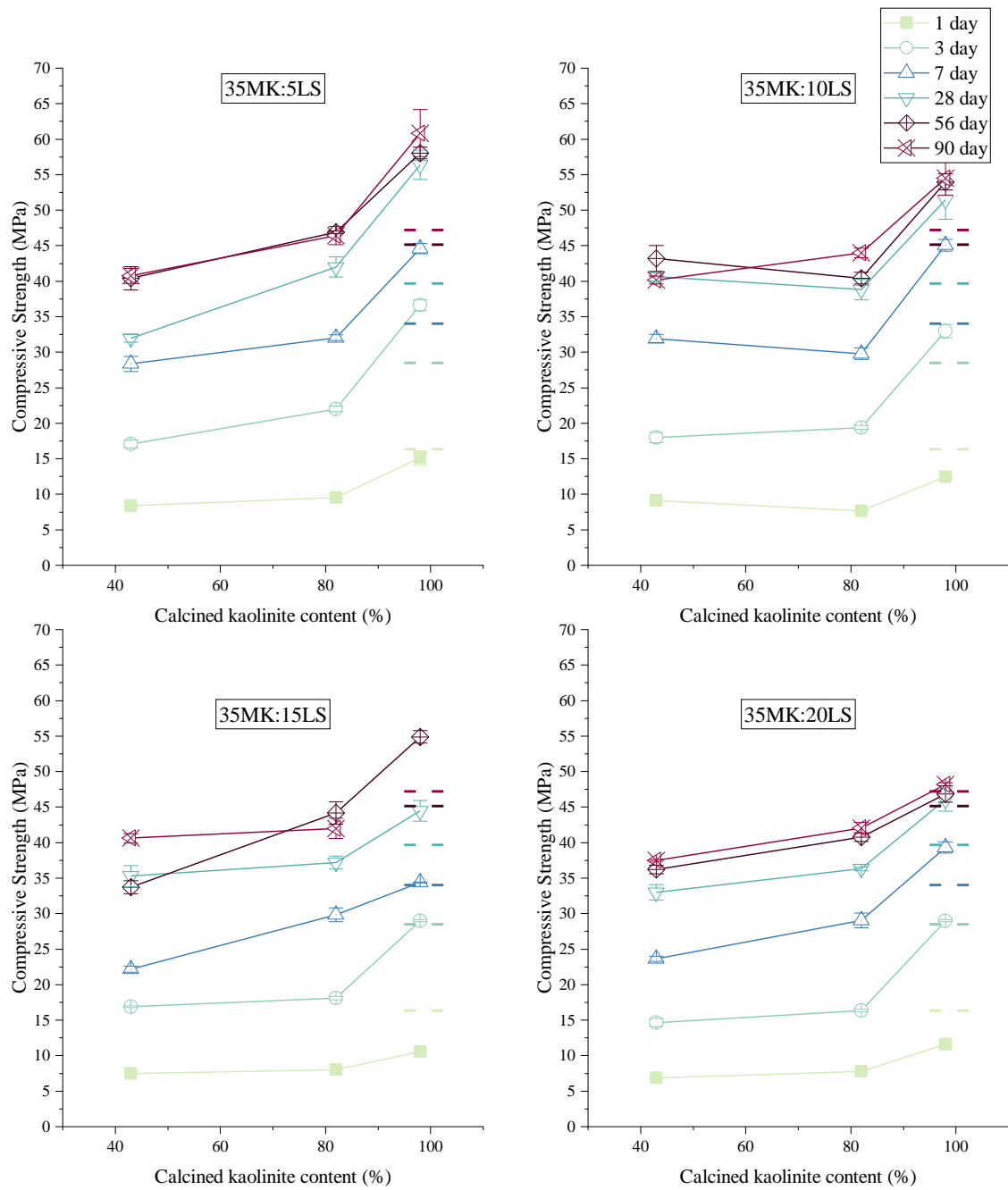
The replacement ratio of 35% by weight of cement with a set of 3 calcined clays and varying content of calcined kaolinite (i.e., metakaolin) and limestone was studied across all combinations with a constant water-to-binder ratio of 0.45. Compressive strength of mortar cubes containing metakaolin and limestone following the mix proportions described in Table 3.6 are shown in Figure 3.3 for 1, 3, 7, 28, 56, and 90 days. Mortars made with 100% PC show higher compressive strength at 1 day, but lower values are observed at later ages (i.e., 7 days onwards) as it is surpassed by mortars containing calcined clay K0 and limestone for all mixes studied (i.e., 35MK with 5LS, 10LS, 15LS, 20LS). This indicates that for clays with high content of calcined kaolinite clay (i.e., above 90%) the pozzolanic reaction takes place after 3 days of hydration and becomes dominant after 7 days of casting. Special attention is brought to blends 35MK:15LS and 35MK:20LS which correspond to the blends with the highest total replacement ratios (50% and 55% of cement substitution respectively). For blend 35MK:15LS, values of compressive strength were 12% and 22% greater than PC mortars (i.e., Control mix) at 28 and 56 days respectively. At a higher replacement ratio, 35MK:20LS mortar was 16% stronger than the Control mortar mix at 28 days and presented very similar values at 56 days which confirms the synergistic effect of MK and LS and its effect on cement hydration and strength evolution.

Mortars containing calcined clays with moderate-to-high content of calcined kaolinite (i.e., K1 = 82%) showed very similar compressive strength to that of the Control mix at 7 days of casting for all of the mixes with varying ratios of limestone. Furthermore, compressive strength of the Control mix was surpassed by the mix 35MK:5LS (i.e., total cement replacement of 40%) made with this clay after 28 days onwards and by mix 35MK:10LS (i.e., total clinker replacement of 45%) after 90 days. Contrastingly, none of the mortars made with calcined clays comprising low-to-moderate calcined kaolinite content (i.e., K2 = 43%) showed higher compressive strength than that of the Control mix at any of the ages studied. However, comparable values were achieved for mixes containing 5% and 10% limestone (i.e., 35MK with 5LS, 10LS) after only 3 days of casting which demonstrates the feasibility of using a wider range of calcined clays with varying calcined kaolinite content, including those considered as *low-grade* calcined clays in higher coupled substitution ratios with limestone (total substitution of 40% and 45% of clinker). The effect of the variation in LS content in compressive strength is also observed. Mortar blends with a composition of 35MK:5LS showed the highest values of strengths for all the dates analyzed. A similar behavior is observed for mix 35MK:10LS with a higher total replacement ratio which allows for a greater potential reduction of emissions compared to portland cement mixes. Identical trends in the evolution of compressive strength of mortar mixes with 35% metakaolin replacement of varying calcined kaolinite content and different limestone content (i.e., 5%, 10%, 15%, and 20%) is displayed in Figure A. 1 of the Appendix section.



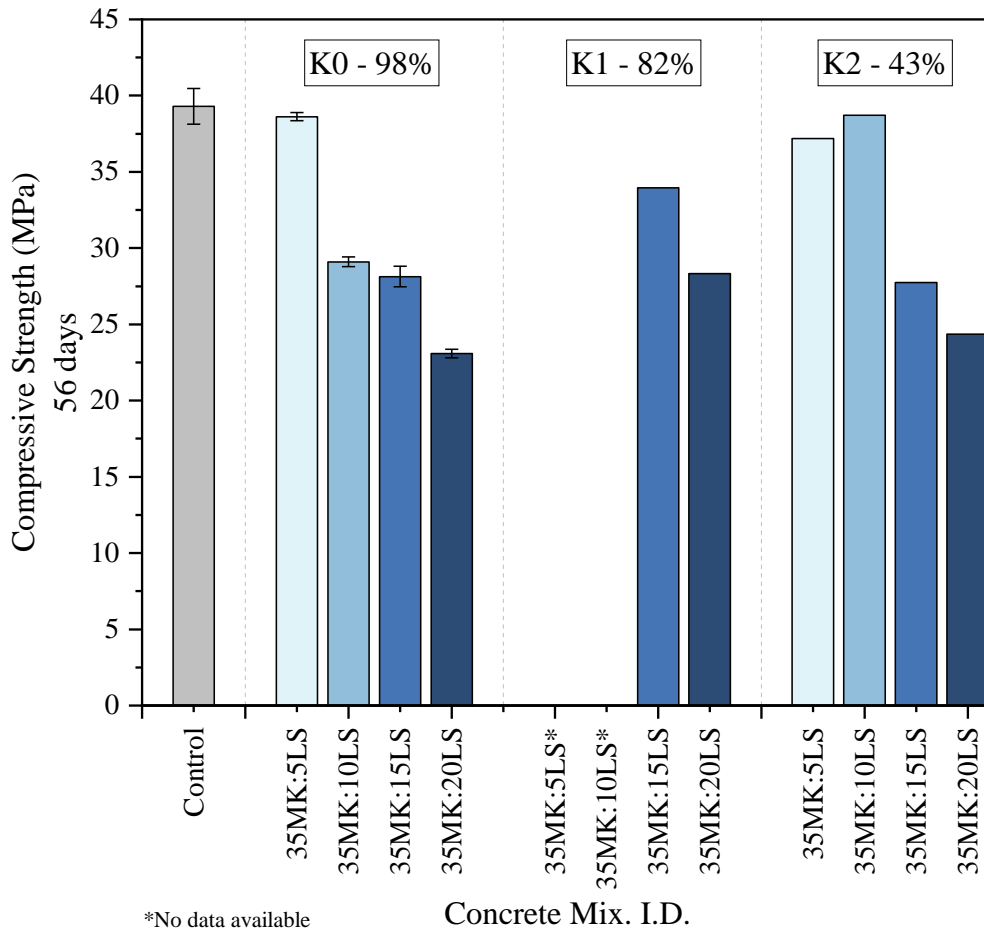


**Figure 3.3** – Evolution of compressive strength of mortar mixes with 35% metakaolin replacement of varying calcined kaolinite content (i.e., K0 = 98%, K1 = 82%, and K2 = 43%) and different limestone content. The *Control* mix with 100% portland cement is also displayed.



**Figure 3.4** – Compressive strength of mortar mixes with 35% metakaolin replacement of varying calcined kaolinite content and different limestone content (i.e., 5%, 10%, 15%, and 20%). Dotted lines indicate Control strengths for each day of testing.

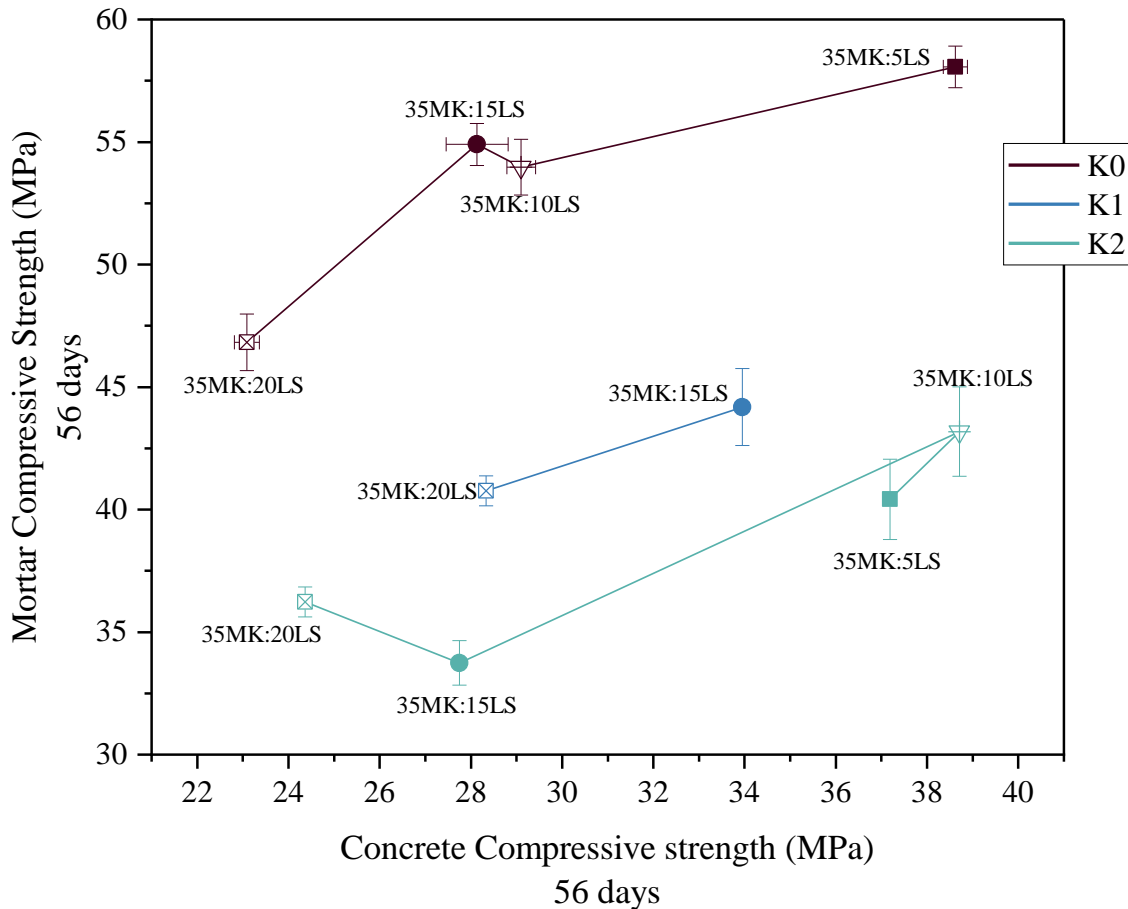
In Figure 3.4, the compressive strength of each of the mortar mixes is shown as a function of the calcined kaolinite content of the calcined clays under study (K0, K1, and K2) for each day of testing (i.e., 1, 3, 7, 28, 56, and 90 days). Although the compressive strength of the mixes studied herein did not increase in a linear fashion with the increased calcined kaolinite content of the clays as previously shown by [94], it is noticeable that the calcined kaolinite clay content is an important factor in determining the strength evolution of mortars made with high replacements of cement with metakaolin and limestone. Compressive strength values of concretes made with plain PC are shown in dotted lines for each day of testing. As mentioned above, mixes with K0 clay showed higher values of compressive strength relative to the those of PC after 3 days of hydration. At later ages (28 and 56 days of hydration), all the blends made with K1 clay exceeded the strength reported by PC in the Control mix and similar values to those of the Control mix were obtained for mortars made with K2 regardless of the substitution level after 56 days.



**Figure 3.5** – 56-day compressive strength of concrete mixes with varying limestone content and different calcined kaolinite content and *Control* as the reference mix with 100% portland cement.

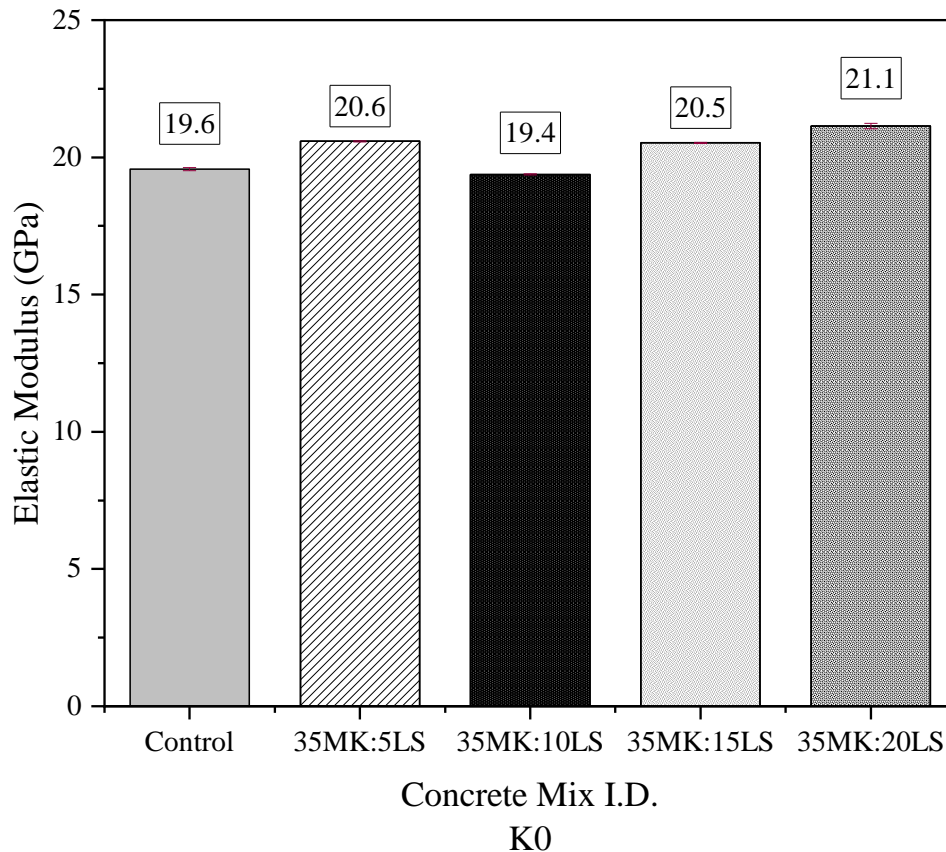
Concrete cylinders of 101.6-mm (4-in) diameter and 203.2-mm (8-in) of height made with the same substitution ratios of metakaolin and limestone were tested under compression and the

results are shown in Figure 3.5. Concrete made with unblended PC (i.e., Control) is also detailed in the figure. Due to limited material supply, only mixes 35MK:15LS and 35MK:20LS were cast with calcined clay K1 and cylinders made with K1 and K2 clays were only tested at 56 days. For all concretes at 56 days, an increase in the overall substitution level yielded lower values of compressive strength regardless of the grade of the calcined clay. Compressive strength results of concrete mixes made with K0 calcined clay and Control mixes are available for additional dates (i.e., 1, 3, 7, 28, and 90 days) in Figure A. 2 in the Appendix section. Concretes made with K0 calcined clay showed decreased strength values with increased limestone content (i.e., above 15% LS) in a similar fashion as the mortars made with the same mixes and calcined clay. The 56-day compressive strength of mortars mixes made with K0, K1, and K2 as a function of the 56-day compressive strength of the concretes made with the same materials and substitution ratios are plotted in Figure 3.6. Results are in agreement with previous findings indicating that compressive strength is mostly influenced by the total replacement percentage of clinker with SCMs and by the calcined kaolinite content of the clay.



**Figure 3.6** – 56-day mortar vs concrete compressive strength of mixes with varying limestone content and different calcined kaolinite content (i.e., K0 = 98%, K1 = 82%, and K2 = 43%).

Due to limited availability of K1 and K2, the static elastic modulus was only obtained for all concrete mixes containing K0 calcined clay. The elastic moduli of all mixes were measured at 28 days and shown in Figure 3.7. The elastic modulus of the reference concrete mix containing 100% PC is also detailed for comparison. The results indicated that all mixes containing metakaolin and limestone, except for 35MK:10LS, showed higher values of elastic moduli than that of concrete made with 100% PC, giving further evidence that concretes made with calcined clay and limestone, even at higher replacement ratios (i.e., 55% total binder replacement) could have similar structural applications than the more conventional concretes made with PC with equivalent strength targets.

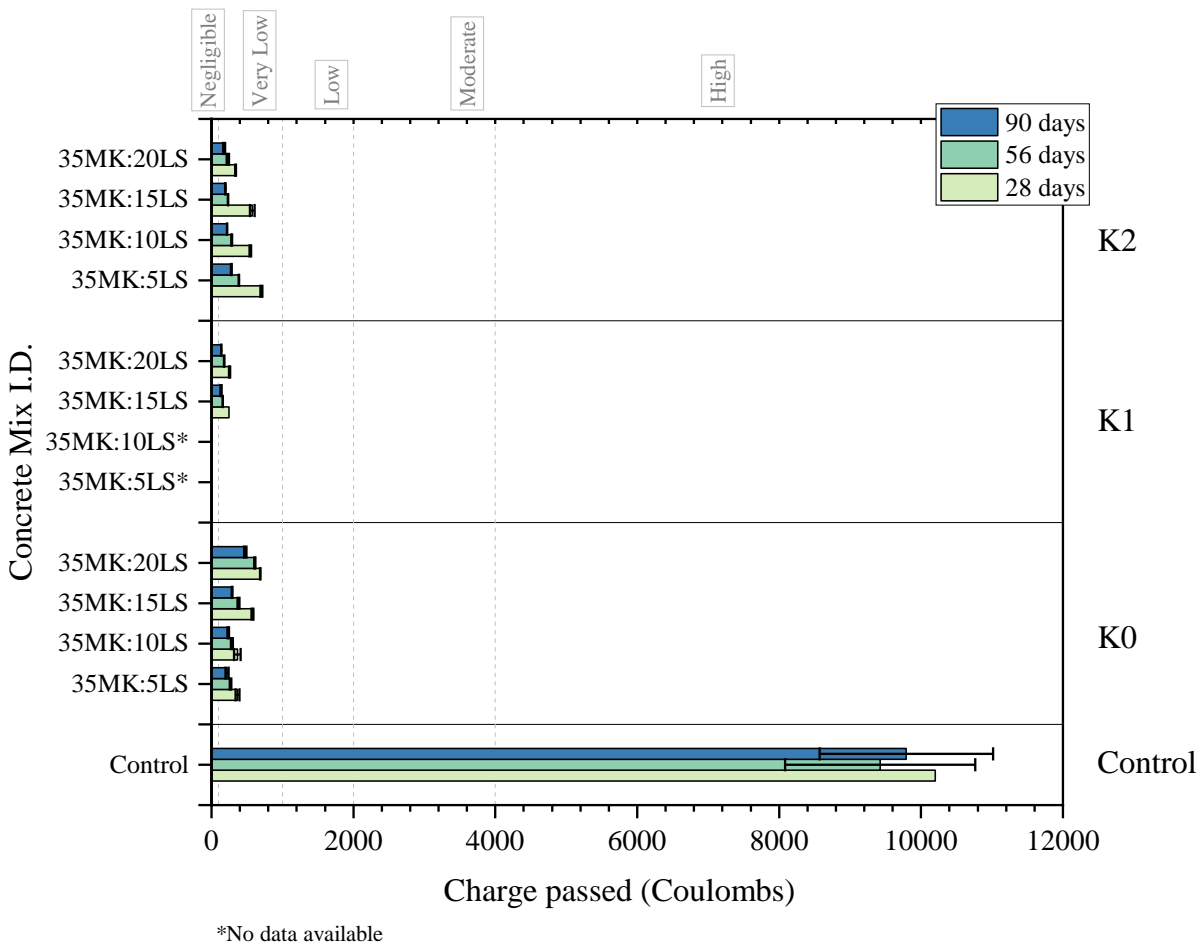


**Figure 3.7** – Elastic moduli of concrete mixes made with high-grade calcined clay (K0 = 98%). Elastic modulus of the reference concrete mix (i.e., Control) is shown for comparison.

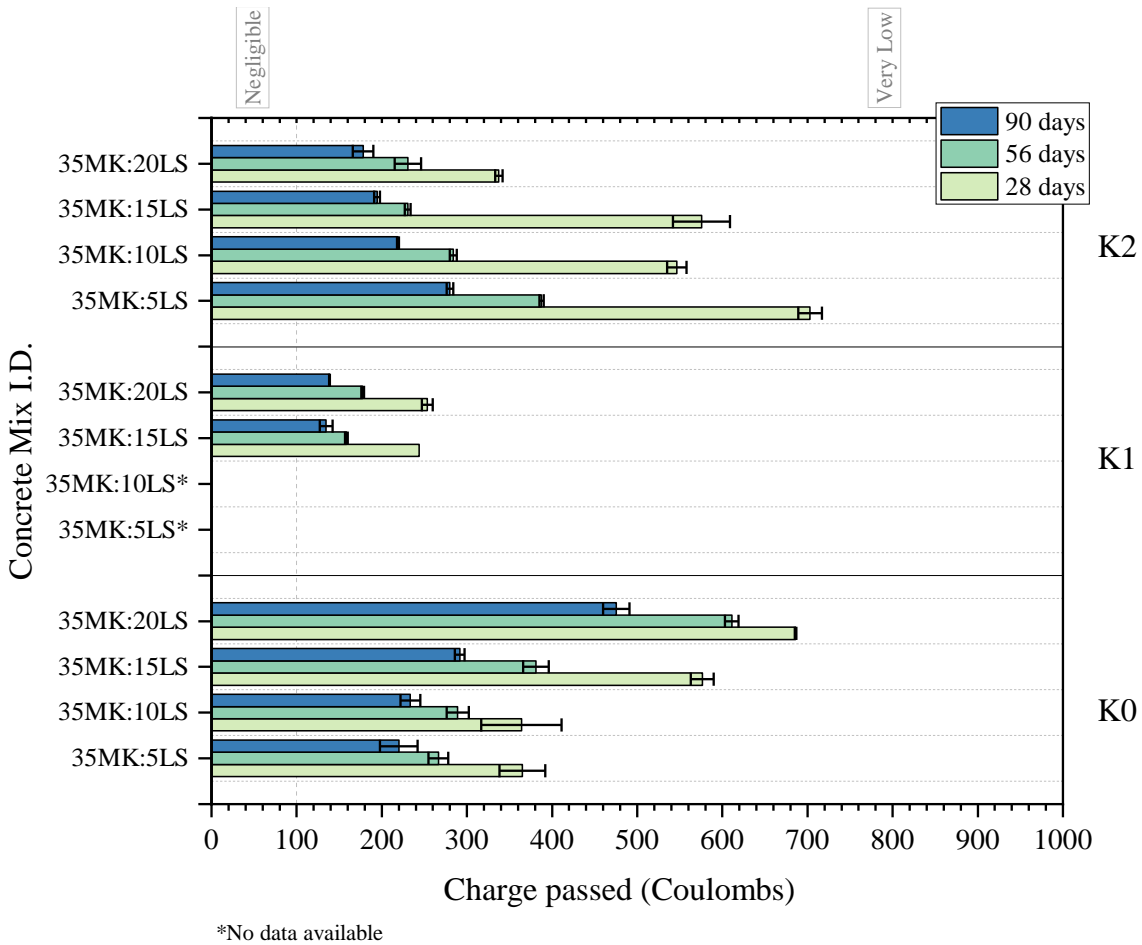
### 3.5.2 Resistance to Chloride Ingress

Resistance to chloride penetration in concrete mixes with metakaolin and limestone at 28 days, 56 days, and 90 days compared to the reference mix made with 100% portland cement is shown for each specimen and each calcined clay studied (i.e., K0, K1, and K2) in Figure 3.8. When no supplementary cementitious materials are used in the concrete mix design (i.e., Control mix), the charge passed for each day of testing is above 4,000 coulombs. According to ASTM C1202, a

charge passed that is higher than 4,000 coulombs indicates a *very high* chloride ion permeability. This is of special interest due to the w/c of 0.57, which is not too high. In contrast, all the concrete mixes containing metakaolin and limestone showed a *very low* chloride ion permeability (1,000-100 coulombs) regardless of the calcined kaolinite content of each clay under study. These results confirm that calcined clay and limestone contribute to the formation of secondary hydration products that lead to a pore refinement at early ages in contrast to the mixes containing only portland cement. The potential for more nucleation sites to be formed could also explain the better performance of these ternary blends at early ages as confirmed by XRD and TGA results of similar blends with calcined clay and limestone previously reported in [42, 104, 105]

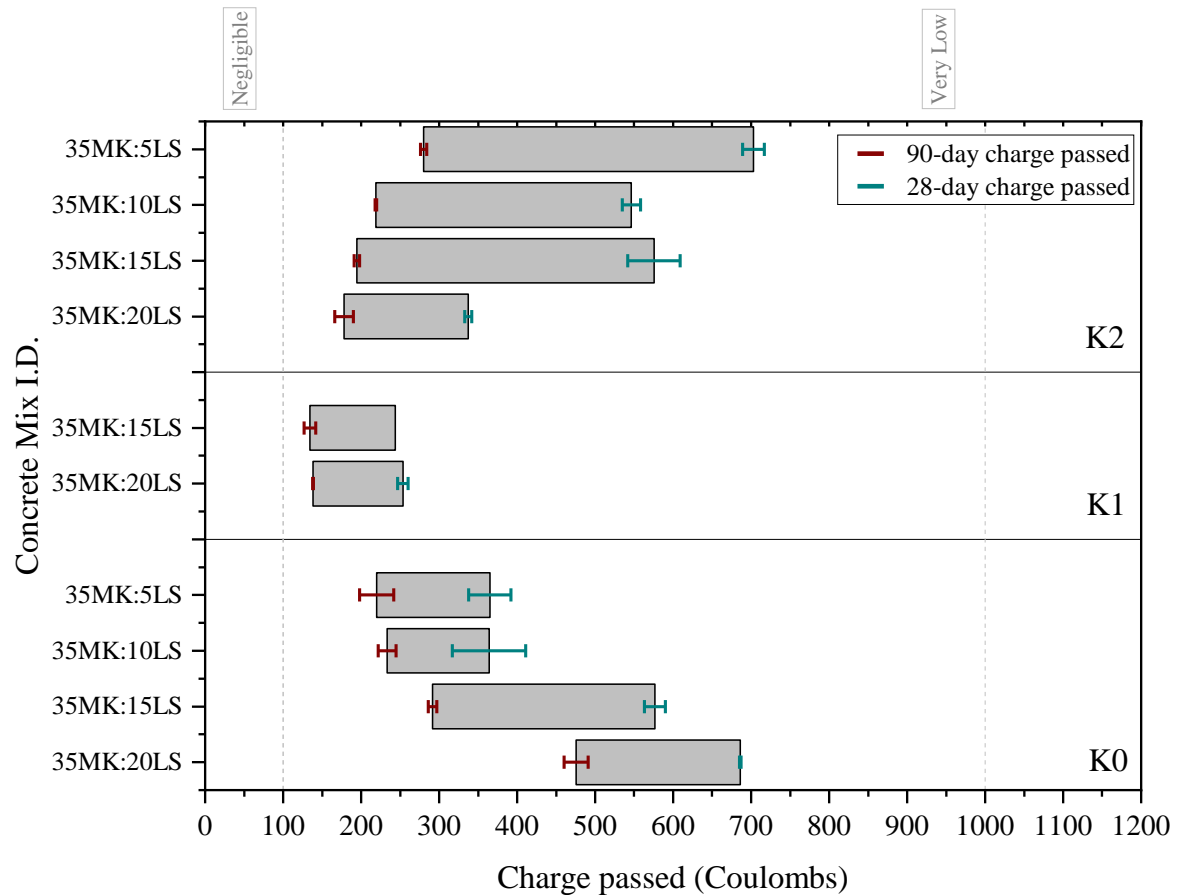


**Figure 3.8** - Charged passed after 28, 56, and 90 days of casting for concrete mixes with varying limestone content and different calcined kaolinite content and *Control* as the reference mix with 100% portland cement.



**Figure 3.9** - Charged passed after 28, 56, and 90 days of casting for concrete mixes with varying limestone content and different calcined kaolinite content (i.e., K0 = 98%, K1 = 82%, and K2 = 43%).

Figure 3.9 details the charge passed through the concrete mixes with blended cement for 28 days, 56 days, and 90 days of hydration. For all of the blends containing MK and limestone, the charge passed decreased with time indicating a densification of the matrix due to the pore refinement action of metakaolin and limestone combined. The decreased charge passed with time could also be explained due to the binding mechanism of chloride ions to the aluminates from the metakaolin as detailed by [54]. Due to limitations in material acquisition, blends with 10% and 5% limestone with 35% MK (i.e., 35MK:10LS and 35MK:5LS) were not studied for the calcined clay with 82% calcined kaolinite content (K1).

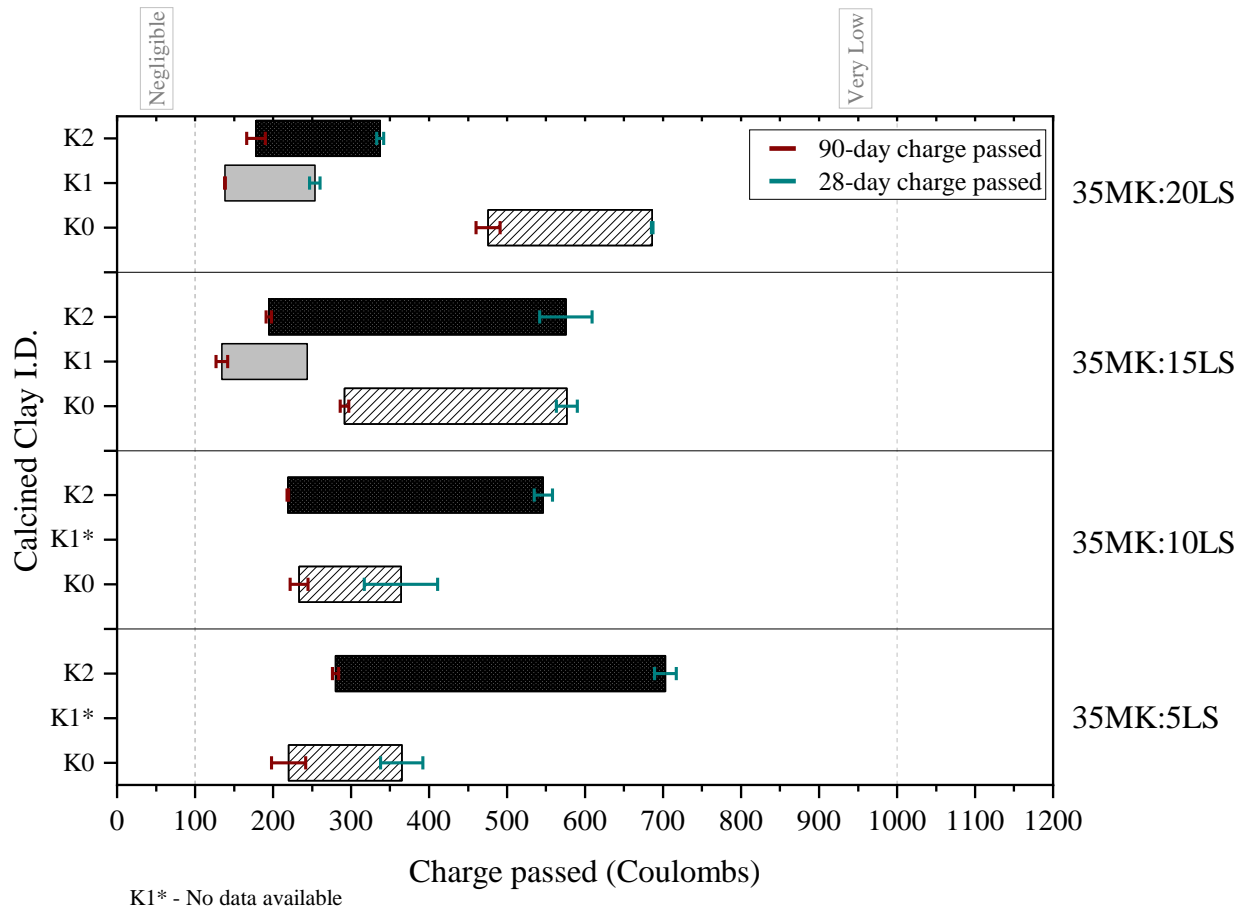


**Figure 3.10** - Charge passed for concrete mixes containing varying content of limestone and a fixed content of metakaolin with varying calcined kaolinite content (i.e., K0 = 98%, K1 = 82%, and K2 = 43%) at 28 days and 90 days after casting.

The results at 28 and 90 days for all concrete mixes with blended cements are arranged by concrete mix I.D. in Figure 3.10 and by calcined clay in Figure 3.11. Even though all of the concrete mixes with cement blends fall into the *very low* category, the total amount of charge passed varied with the calcined kaolinite content of each clay studied. The concrete mixes with calcined clay K0 had minimal charge passed when only 5% to 10% of cement substitution with limestone was used for a total replacement ratio ranging from 40% to 45%, whereas concretes with lower grade calcined clay (i.e., K2) showed higher resistance to chloride penetration at later ages (i.e., 90 days) for higher substitution ratios of 15% and 20% limestone for a total replacement content of 50% to 55%. In addition, similar trends were observed in mixes with a moderate-to-high calcined kaolinite content (i.e., K1 = 82%) especially in those mixes with higher content of limestone and higher overall replacement ratios of clinker. This could indicate that clays with lower contents of calcined kaolinite are most suitable for combinations with higher limestone content which in turn increases the reduction in the clinker-to-cement ratio. Work done by [55] in the chloride transport properties of LC<sup>3</sup> with various kaolinite contents concluded that clays with moderate content of kaolinite mineral (40-50%) were enough to reduce the diffusivity of the matrix by two orders of magnitude compared to PC, thus, demonstrating the applicability of a wider range

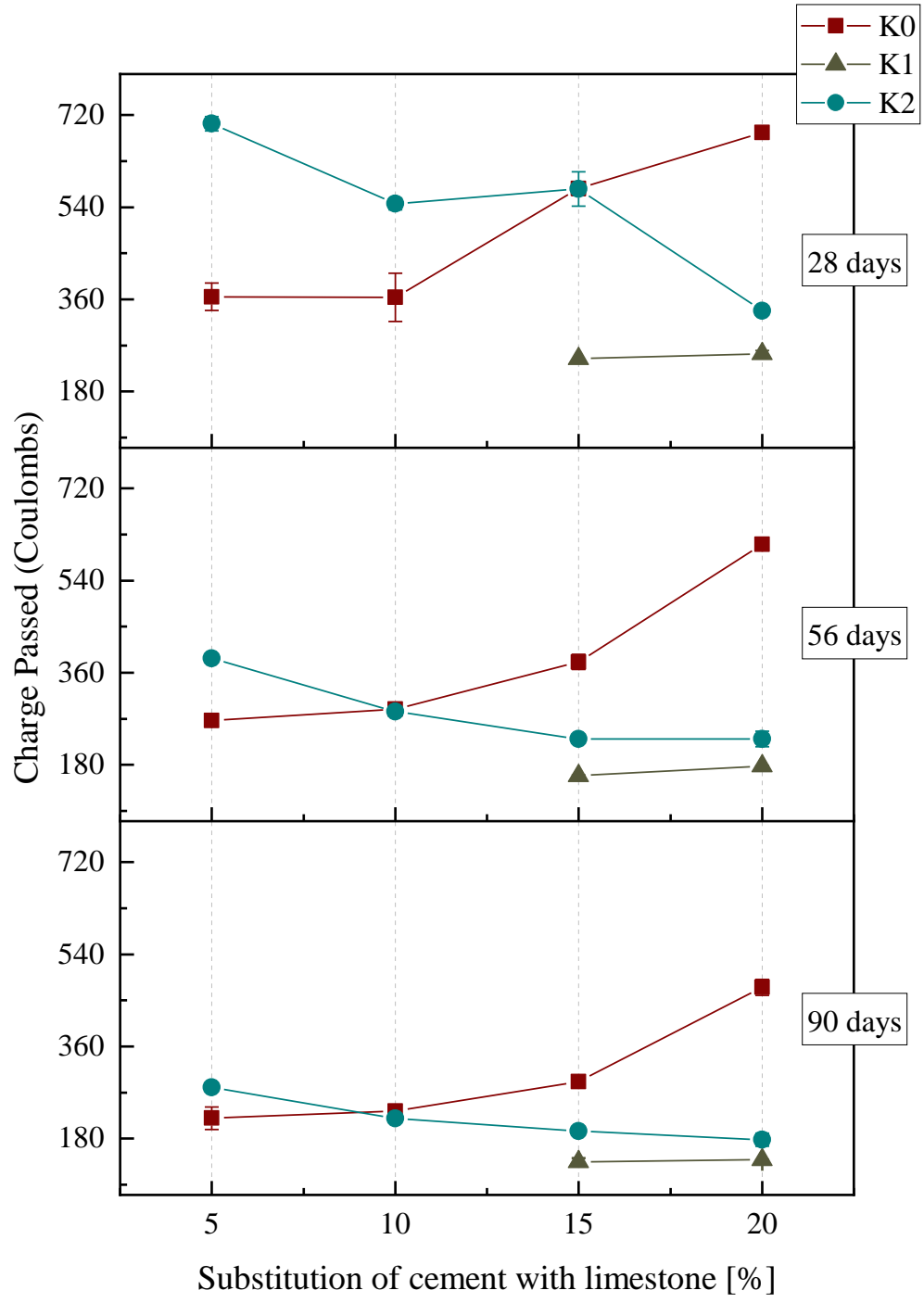


of clays with kaolinite contents lower than 95% (which are often expensive) and supporting the findings obtained from these RCP tests. Furthermore, Figure 3.12 displays the charge passed versus the limestone content for each blend studied. It is clear that concrete mixes with K0 calcined clay had an increase charge passed with an increased content of limestone for all days tested (i.e., 28, 56, and 90 days). In contrast, concrete mixes with the same mix designs and equal replacement ratios made with calcined clay K2, whose calcined kaolinite content is 43% approximately, showed the opposite behavior for all the dates studied (i.e., decreased charge passed with increased limestone content).



**Figure 3.11** - Charge passed for concrete mixes with a fixed content of metakaolin with varying calcined kaolinite content (i.e., K0 = 98%, K1 = 82%, and K2 = 43%) and varying content of limestone and at 28 days and 90 days after casting.

It is also worth noting that even though the pH of the pore solution in cement blends with MK is reduced with the consumption of CH, the rate of chloride binding and the reduction in permeability indicates a great potential in protecting the overall concrete from chloride-induced corrosion in reinforcing steel for reinforced concrete applications. Lastly, results from the RCPT showed a good correlation with the results from the concrete mechanical properties under compression loading revealing positive effects on the mechanical and durability performance of mortars and concretes made with these binders.



**Figure 3.12** - Charge passed vs. limestone content for concrete mixes with 35% replacement with metakaolin at 28 days, 56 days, and 90 days.

### 3.6 Conclusions and Future Research

The experimental plan described in this chapter was designed to study the effect of varying metakaolin to limestone ratios in the mechanical and durability performance of ternary blends made of a combination of portland cement, metakaolin, and limestone. The use of high purity metakaolin (calcined kaolinite mineral content  $\geq 90\%$ ) in combination with limestone has proven to perform very similar to portland cement mixes with equal water cement ratio. However, deposits of suitable clays worldwide present variations in their content of kaolinite mineral. Three different metakaolin clays with varying calcined kaolinite content (i.e., 43%, 82%, and 98%) were used in the set of experiments with a fixed substitution level of 35% by weight of binder. In addition, co-substitution with varying ratios of limestone (i.e., 5%, 10%, 15%, and 20%) were assessed. The results from standard compressive strength tests have proven that a synergistic effect between metakaolin and limestone contribute to a high compressive strength for mortars after 7 days of hydration despite the content of calcined kaolinite mineral of the calcined clays. More specifically, the following conclusions can be drawn:

- High-grade metakaolin (K0) surpassed compressive strength of PC concrete already after 3 days of hydration showing the rapid action of pozzolanic reaction for these types of SCMs even at higher replacement ratios (i.e., 50% and 55% of clinker substitution).
- For low-grade calcined clays with a calcined kaolinite content lower than 45%, comparable values to those from PC mortars were achieved for co-substitution of 35% metakaolin and 5-10% of limestone (i.e., 35MK with 5LS, 10LS) after only 3 days which demonstrates the feasibility of using a wider range of calcined clays with varying calcined kaolinite content, even at higher coupled substitution ratios with limestone (total substitution of 40% and 45% of clinker). For this reason, the calcined kaolinite clay content is an important factor in determining the strength evolution of mortars made with high replacements of cement with metakaolin and limestone.
- For concrete mixes with the same mixes and substitution levels formulated for mortar, an increase in the overall substitution level yielded lower values of compressive strength regardless of the grade of the calcined clay after 56 days of casting.
- all mixes containing K0 metakaolin and limestone showed higher values of elastic moduli than that of concrete made with 100% PC, giving further evidence that concretes made with calcined clay and limestone, even at higher replacement ratios (i.e., 55% total binder replacement) could have similar structural applications than the more conventional concretes made with PC with equivalent strength targets and water-to-binder ratio.
- Potential for chloride-induced corrosion was determined by means of RCP tests. All of the concrete mixes containing metakaolin and limestone showed a very low chloride ion permeability (1,000-100 coulombs) regardless of the calcined kaolinite content of each clay under study. These results confirmed that calcined clay and limestone contribute to the formation of secondary hydration products that lead to a pore refinement at early ages in contrast to the mixes containing only portland cement. Moreover, for all of the blends containing MK and limestone, the charge passed decreased with time indicating a densification of the matrix due to the pore refinement action of metakaolin and limestone combined. The decreased charge passed with time could also be explained due to the binding mechanism of chloride ions to the aluminates from the metakaolin. When

comparing calcined kaolinite contents of different clays, RCPT suggested that clays with lower contents of calcined kaolinite are most suitable for combinations with higher limestone content which in turn increases the reduction in the clinker-to-cement ratio

Finally, the experimental plan demonstrated the robustness of ternary cement blends composed of cement, calcined clay, and varying ratios of limestone, even for lower grades of calcined clay (i.e., low calcined kaolinite content). The compressive strength results showed comparable mechanical performance than that of mortars and concretes made with 100% portland cement. Furthermore, the transport properties are outstandingly improved with respect to those from portland cement concretes which translate into more durable cement binders. The development of ternary blends made with portland cement, calcined clay, and limestone at industrial scale will have the potential to contribute to the global mitigation of greenhouse gas emissions from the cement and concrete industry worldwide. The effects on mechanical and durability properties of these mixes with other sources of calcite-rich materials different from limestone (i.e., dolomite, marble stone, etc.) were out of the scope of this study but should be explored. Additionally, further investigation in the wide scale implementation of calcined clay and limestone in cement-based binders could solidify the benefits of using these materials, especially as they offer promising low-carbon cement alternatives for emerging economies and developing countries where high investment costs are a limitation to the successful implementation of other highly technical solutions such as carbon capture and storage.

# **Chapter 4 – Development of MKC-LCA Tool to Compute the Environmental Impacts of Calcined Clay in Cement and Concrete**

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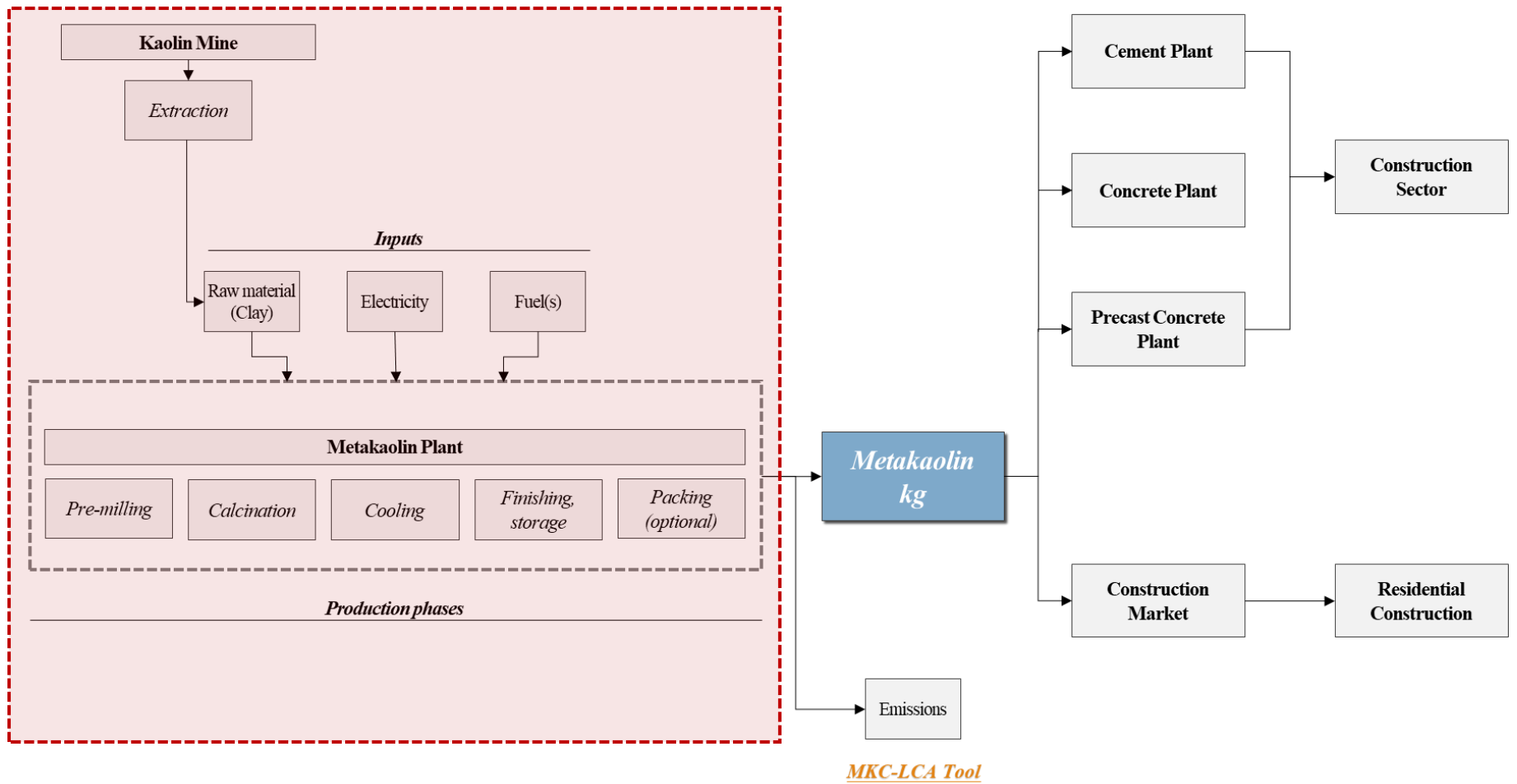
The first step to conduct the life-cycle assessment (LCA) of metakaolin, is to build the life-cycle inventory (LCI) of energy use, resources, and consumption indices along the value chain of the material. This step is necessary to evaluate the environmental profile of calcined clays in cement and concrete applications. As discussed in Chapter 2, metakaolin has been incorporated in reported values of Global Warming Potential (GWP) of concrete mixes [23, 34, 39, 70-73, 75, 106] but the individual contribution of this material is still unclear and conflicting values have been pointed out by other authors such as Habert and Ouellet-Plamondon [23]. This section provides a description of the MKC-LCA Tool designed to estimate the environmental performance of metakaolin production from cradle to gate based on real (local) parameters. The life-cycle assessment was organized following the four major phases of the International Organization for Standardization (ISO) LCA 14040:2006 and 14044:2006 Standards: (1) goal and scope definition, (2) inventory analysis, (3) impact assessment, and (4) interpretation [107, 108] which are described in detail herein. With this tool, cement/concrete manufacturers, decision makers in the construction sector, and researchers can obtain a real validation of the benefit of implementing metakaolin in their mix designs. Results from the tool can easily be included in the life-cycle assessment of concrete mixes by considering whether the inclusion of metakaolin occurs at the cement level (i.e., combined with clinker and other supplementary cementitious materials to produce blended cements) or at the concrete level (i.e., incorporated in the concrete mix at the concrete batching and mixing stages). Life-cycle emissions and materials consumption from all the activities related to the cement and concrete manufacturing must be included for a complete analysis. Chapter 5 presents case studies showing how the results from the MKC-LCA Tool are included in the total life-cycle assessment of real mortar and concrete mixes to assess their environmental impact compared to those made with 100% portland cement.

## **4.1 Structure of the MKC-LCA Tool**

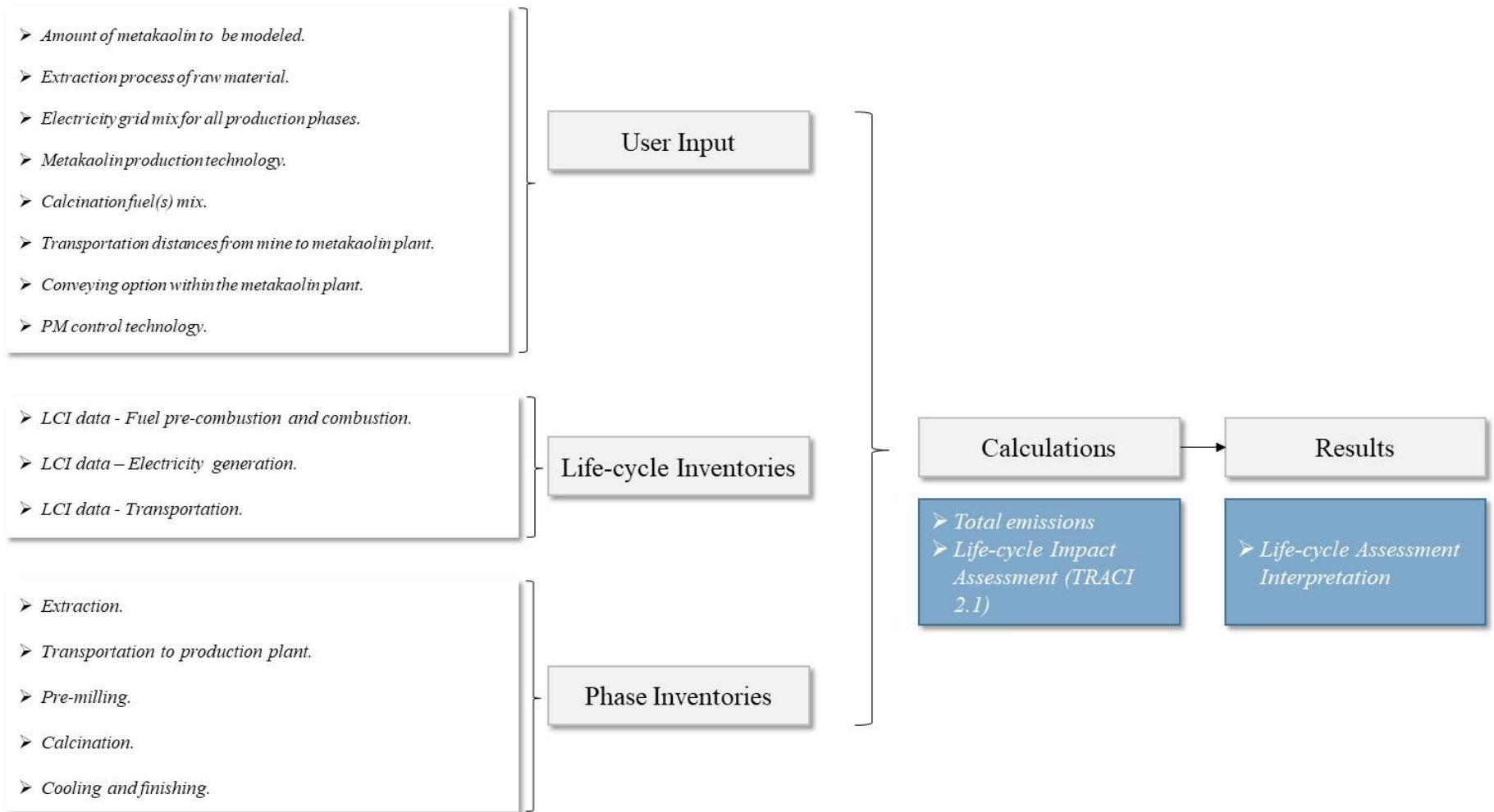
### **4.1.1 System Boundary and Modeling Parameters**

The MKC-LCA Tool is an excel-based tool that focuses on the production of metakaolin in a mass basis, where the functional unit to be modeled is kilograms of metakaolin. The analysis ends at an intermediate stage of metakaolin's life-cycle (i.e., cradle to gate) which is a widely accepted end point for the assessment concrete and other building materials. However, this type of analysis is very useful to develop complete life-cycle assessments of concrete in buildings and other applications. Figure 4.1 shows the system boundary of MKC-LCA Tool. Each sheet within the tool can be grouped into three big categories: User Input Data, Life-Cycle Inventories, and Phase Inventories. Inputs defined by the user are then used to obtain the phases inventories which in turn are multiplied by the life-cycle inventory of emissions from fuel (pre-combustion and combustion), electricity generation, and transportation to finally obtain the total emissions from metakaolin production. Figure 4.2 presents a summary of the structure of the MKC-LCA Tool.

The following sections detail each of the main categories of data described above as well as the references and main sources of information used to feed each sheet and to allow for calculations of total emissions. Once the total emissions have been computed, the life-cycle impact assessment of the functional unit to be modeled by the user is performed following the methodology proposed by the U.S. Environmental Protection Agency (EPA) in their Tool for Reduction and Assessment of Chemical and Other Environmental Impacts (TRACI) [109].



**Figure 4.1** – The red box shows the system boundary of MKC-LCA Tool.



**Figure 4.2** - MKC-LCA Tool structure.



### 4.1.2 The User Input Sheet

The *User Input* sheet is an interactive tool for the user to calculate the life-cycle environmental impact of metakaolin production. The sheet has eight categories with drop down menus that allow the user to input parameters according to their location, method of extraction, electricity grid mix used, technology process, and fuel mix used for clay calcination.

#### 4.1.2.1 Modeling Parameters

In this section, the user can input the total amount of metakaolin to be modeled and the name of the model. See Figure 4.3.

| Modeling Parameters |                                  |
|---------------------|----------------------------------|
| Functional Unit     | Kilograms of metakaolin          |
| System Boundary     | Cradle to gate                   |
| Unit Type           | mass                             |
| Unit                | kg                               |
| Total Amount        | 1                                |
| File Name           | Metakaolin analysis - Green Inc. |

Figure 4.3 - MKC LCA Tool. User Input sheet. Modeling Parameters.

#### 4.1.2.2 Extraction Process Input

Extraction of the raw kaolin clay for metakaolin production is the first step within the metakaolin manufacturing process. Extraction of clays for the production of cement-based materials is generally performed by means of open pit extraction typically achieved with hydraulic excavators and front-end loaders. The material is subsequently transported by truck to the production plant, which usually is located within close proximity to the mining site of the raw material. Detailed life-cycle inventory data of energy use (electricity and fuels), water consumption, and air emissions are described in Section 4.1.4.1.

#### 4.1.2.3 Electricity Grid Mix Input

This section allows the users to select the electricity grid mix of each phase of production according to their location. The drop-down menu contains the 50 U.S. states as well as the U.S. average option. When the location is outside the U.S. and the fuel percentages for the electricity grid mix is known by the user, the input *User\_specific\_grid\_mix* is available to the user. The tool allows for up to 3 user-defined options. See Figure 4.4.

| Electricity Grid Mix Input   | [Please select the location for each processing stage] |
|--|--|
| Electricity mix for kaolin extraction (mining)   | AL   |
| Electricity mix for kaolin processing and calcination (at metakaolin production plant) | AL   |

**Figure 4.4** - MKC LCA Tool. User Input sheet. Electricity grid mix input.

#### 4.1.2.4 Electricity Grid Mix User Specific

The user can input up to three user-defined options when the location of the phases of production is outside the U.S. and the contribution in percentage of each energy source in the total electricity grid generation is known to the user.

#### 4.1.2.5 Metakaolin Production Technology Option by Phase

The users can input the type of technology used at each stage of the production process of metakaolin. For each process, the user can click the drop-down menu to select the option that best adjusts to their model. Figure 4.5. Section 4.1.4 contains a detailed description on each individual production phase of metakaolin manufacturing and the technology options offered in the tool. Section 4.1.4 also includes inventory data of materials, electricity use, water consumption, and fuel inputs for each production phase as well as process-related emissions.

| Metakaolin Processing                              | Technology Option                                      |
|--|--|
| Raw Material Drying                                | No drying  |
| Raw Material Pre-milling                           | Ball Mill_Dry grinding                                 |
| Raw Material Calcination                           | Dry Rotary Kiln  |
| Calcined Clay Cooling Technology                   | Rotary Cooler  |
| Grinding and Blending with Portland Cement Clinker | Separate grinding - interblending with portland cement |
| Calcined Clay Grinding Technology                  | Ball (Tube) Mill                                       |

**Figure 4.5** - MKC LCA Tool. User Input sheet. Production technology.

For each production phase, Table 4.1 shows the different technology options available to the user in the MKC LCA Tool.

**Table 4.1** – MKC LCA Tool. Technology options for metakaolin processing.

| <b>Metakaolin Processing – Technology Options</b> |                                 |   |  |  |
|---|---------------------------------|---|--|--|
| <b>Raw Material Pre-milling</b>                   | <b>Raw Material Calcination</b> | <b>Calcined Clay Cooling Technology</b>   | <b>Grinding and Blending with Portland Cement</b>      | <b>Calcined Clay Grinding Technology</b> |
| Ball Mill_Dry grinding                            | Flash Calciner                  | Rotary Cooler                             | Separate grinding - interblending with portland cement | Ball (Tube) Mill                         |
| Tube Mill_Dry grinding                            | Vertical Calciner               | Planetary Cooler                          | Intergrinding with clinker                             | Horizontal Roller Mill                   |
| Vertical Roller Mill_Dry grinding                 | Dry Rotary Kiln                 | Travelling Grate Cooler                   | Not blended - mixed in at the concrete plant           | Roller Press                             |
| No_Pre-grinding                                   | Wet Rotary Kiln                 | Reciprocating Grate Cooler (Conventional) |  | Vertical Roller Mill                     |
|   |                                 | Reciprocating Grate Cooler (Modern)       |  |  |
|   |                                 | Vertical Gravity Cooler with Grate Cooler |  |  |

#### **4.1.2.6 Metakaolin Calcination Fuel Mix Input**

This section of the tool allows the user to input the fuel mix that is used for the clay calcination process. A drop-down menu allows the user to select the *User\_specific\_fuel\_mix* when the fuel mix is known, or the *U.S. average fuel mix* when the fuel mix is not known but the user still wants to get a complete assessment of the material modeled. For each fuel source, the user can enter the corresponding percentage as seen in Figure 4.6.

## Metakaolin Calcination Fuel Mix Input

User\_specific\_fuel\_mix

| Fuel Options for Calcination  | [%]   |
|-------------------------------|-------|
| Bituminous coal               | 91.0% |
| Lignite coal                  | 0.0%  |
| Petroleum coke                | 0.0%  |
| Natural gas                   | 0.0%  |
| Residual (heavy) fuel oil     | 0.2%  |
| Distillate (Diesel) fuel oil  | 0.8%  |
| Waste oil                     | 0.3%  |
| Waste solvent                 | 4.0%  |
| Waste tire (whole)            | 1.8%  |
| Waste tire (shredded)         | 1.8%  |
| Waste paper (cardboard, wood) | 0.0%  |
| Waste plastics                | 0.0%  |
| Waste sewage sludge (dry)     | 0.0%  |
| Waste (other/non-hazardous)   | 0.0%  |
| Waste (other/hazardous)       | 0.0%  |
|                               | 100%  |

Figure 4.6 - MKC LCA Tool. User Input sheet. Calcination fuel mix.

The percentages of the U.S. average fuel mix input for clinker production and kiln firing are the options available as default in the MKC-Tool. Percentages for the U.S. average fuel mix are shown in Table 4.10 from Section 4.1.4.4.

### 4.1.2.7 Transportation Input

To account for impacts associated with transportation of raw and finished materials throughout the system boundary, the user can define the transportation modes and the traveled distances for different phases including transportation from the extraction site to the metakaolin production plant, transportation from the processing plant to the cement plant (if final product is blended cement and processing of cement and metakaolin occur in different facilities), and the transportation from processing plant to concrete plant (if final product is metakaolin as SCM). In addition, the tool allows for up to three different modes of transportation and traveled distances for the case of multimodal transportation or segmented routes.

|  | Transportation Mode 1       | Distance Traveled (km) |
|--|-----------------------------|------------------------|
| Kaolin (raw clay) from mining site to processing plant   | Truck class 8b (Model 2005) | 100                    |
| Metakaolin (processed clay) from processing plant to cement plant (if final product is blended cement and processing of cement and metakaolin occur in different facilities) | Truck class 8b (Model 2005) | 100                    |
| Metakaolin (processed clay) from processing plant to concrete plant (if final product is metakaolin as SCM)  | Truck class 8b (Model 2005) | 100                    |

**Figure 4.7** - MKC LCA Tool. User Input sheet. Transportation inputs.

#### 4.1.2.8 Conveying Options

Material transport within the production plant from one production station to the another requires the use of mechanical or pneumatic systems typically run with electricity. For each production station, the user can select the type of conveyance technology and the distance travelled by the material for the *raw clay from silos to pre-milling station to finished product to silos or packaging station* as shown in Figure 4.8.

Enter the conveyance technology for each scenario and the distance traveled in m.

|   | Conveyance Technology | Distance (m) |
|---|-----------------------|--------------|
| Kaolin (raw clay) from silos to pre-milling station | Screw pump            | 20           |
| Pre-milled raw clay to the calcination unit         | Screw pump            | 20           |
| Calcined clay to cooling station                    | Airlift               | 20           |
| Calcined clay to grinding station                   | Dense phase pump      | 40           |
| Calcined clay to blending station (optional)        | Bucket elevator       | 20           |
| Finished product to silos or packaging station      | Screw pump            | 20           |

**Figure 4.8** - MKC LCA Tool. User Input sheet. Conveying options.

#### 4.1.2.9 Particulate Matter (PM) Control Technology Option

PM emissions from metakaolin production are originated mainly during (1) mining and crushing, (2) storage, (3) calcination, (4) cooling, and (5) grinding and finishing. For PM emissions associated with each of these production phases for metakaolin production, the user can determine what type of technology is used to control process-related PM emissions at the plant. PM control technology options available in the tool are: fabric filter (FF), electrostatic precipitators (ESP), or uncontrolled emissions. These options are the most common ones implemented in cement plants

where metakaolin production at industrial scale could be incorporated. Figure 4.9 shows the user input selection for process-related PM Control.

| Process-related PM Control     | Technology Option                 |
|--------------------------------|-----------------------------------|
| Clay Pre-milling PM Control    | Fabric Filter (FF)                |
| Clay Calcination PM Control    | Fabric Filter (FF)                |
| Metakaolin Cooling PM Control  | Electrostatic Precipitators (ESP) |
| Metakaolin Grinding PM Control | Pulse Jet Bag Filter (PJBF)       |

**Figure 4.9** - MKC LCA Tool. User Input sheet. Process-related PM control technology options.

#### 4.1.2.10 Results

After all the parameters at each stage of production have been properly entered, the user can press the “Generate Results” button to be directed to the results sheet which contains a summary of the modeling parameters, the air emissions associated with each production phase as well as the impact categories considered relevant to metakaolin LCIA: (1) Global Warming Potential for Air Emissions – 100 year, (2) Acidification Potentials for Air Emissions, (3) Human Health Particulate Potentials for Air Emissions, (4) Eutrophication Potentials for Air Emissions, (5) Ozone Depletion Potentials for Air Emissions, (6) Smog Formation Potentials for Air Emissions, (7) Freshwater Ecotoxicity Potentials for Urban Air Emissions, (8) Human health Cancer Potentials for Urban Air Emissions, (9) Human health Non-cancer Potentials for Urban Air Emissions, and (10) Fossil Fuel Depletion. In addition, the total energy use from electricity demand and fuel use, as well as water consumption are shown in the same sheet. Values are displayed in graphic and tabular format with bar diagrams detailing the system energy use and GWP as well as other relevant impact categories.

#### 4.1.3 Life-Cycle Inventories

Besides the raw materials to produce metakaolin, fuel and electricity are the main resources consumed during metakaolin manufacturing. The MKC-LCA Tool does not only consider direct emissions from metakaolin processing from direct fuel combustion and electricity use, but also takes into account the supply-chain effects of fuel procurement and processing (pre-combustion) and electricity generation (construction and operation of power plants) in its assessment.

For this purpose, a thorough review of current literature and existing databases of emissions associated with fuel pre-combustion and combustion emissions as well as those associated with electricity generation was performed and data were obtained from different studies developed both within the U.S. and internationally in order to generate a complete life-cycle inventory (LCI) of the most common fuels used in metakaolin extraction and production processes as well as an LCI of electricity generation. Due to lack of data published on metakaolin production, when needed, values were adapted from the ones reported by Gursel [110], the Environmental Protection Agency’s Emissions and Generation Resource Integrated Database (E-GRID) [111], the Intergovernmental Panel for Climate Change (IPCC) Guidelines for GHG inventory [112], the U.S. Energy Information Administration – State Energy Data System (SEDS) [113], and other

published LCA studies [114-116]. A description of the data obtained and the calculations and assumptions made are detailed in the following sections.

#### 4.1.3.1 Fuel Pre-Combustion LCI

Values for extraction, processing and delivery of fuels to the quarry or plant were computed by Gursel [110] and based on data from the National Renewable Energy Laboratory (NREL) LCI Data which contains the quantities of different fuels used to extract and processed each fuel used in the tool. Fuel pre-combustion data for ten fuels (fossil and nuclear) available in the MKC\_LCA Tool are compiled in Table A. 1 in the Appendix section. Values on this table were adopted from Table 4.15 by Gursel [110] and contain heating values per fuel source, total pre-combustion energy use and water use in MJ/unit of fuel and kg/unit of fuel processed respectively, as well as solid waste and air emissions generated. Equation (4.1) shows the calculation of emissions associated with fuel pre-combustion activities.

$$Emissions_{output\ pre-c, fuel} = Fuel\ consumption_{fuel} * EF_{output\ pre-c, fuel} \quad (4.1)$$

Where:

|                                   |  |
|-----------------------------------|--|
| $Emissions_{output\ pre-c, fuel}$ | = emissions of each output (e.g., CO <sub>2</sub> , CH <sub>4</sub> , etc.) during pre-combustion by type fuel (kg).           |
| $Fuel\ consumption_{fuel}$        | = amount of fuel combusted (e.g., kg, liters, MJ).   |
| $EF_{output\ pre-c, fuel}$        | = emission factor of an output during pre-combustion by type of fuel (kg output/kg fuel, kg output/l fuel, kg output/MJ fuel). |

The total emissions of a particular output (e.g., CO<sub>2</sub>, CH<sub>4</sub>, etc.) during pre-combustion of the fuels used in the production phases is calculated following equation (4.2):

$$Emissions_{output\ pre-c} = \sum_{fuels} Emissions_{output\ pre-c, fuel} \quad (4.2)$$

Given their nature, emissions associated with energy recovered from waste fuels' combustion are only considered to be direct combustion emissions as there is no allocation of upstream materials and emissions assigned to waste fuels. Only fuel combustion LCI data were taken into account for these types of fuels.

### 4.1.3.2 Fuel Combustion LCI

Fuel combustion LCI emissions for fossil fuels and waste fuels commonly used during the calcination process were adapted from different sources including: Gursel [110], IPCC Guidelines for National Greenhouse Gas Inventory 2006 and its refinement from 2019 [112, 117], and Boesch [13, 114] and compiled in Table A. 2 y Table A. 3. When available, the average value from all sources was adopted. Average (i.e., default) emission factors for each greenhouse gas (e.g., CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O) and each type of fuel were considered following the Tier 1 methodology proposed in the IPCC Guidelines for National GHG Inventory which considers complete oxidation of the carbon contained in the fuel. In actuality, emissions factors from different gases related to the combustion of stationary fuels could vary depending on the type of fuel, the combustion technology, the operating conditions, the control technology, the quality of maintenance, and the age of the equipment used to burn the fuel. Furthermore, these aspects could be country- or region-specific [112]. Equations (4.3) and (4.4) are used to calculate the emissions from stationary combustion of fuels used for energy production in the MKC-LCA tool and data from Table A. 2 and Table A. 3:

$$\mathbf{Emissions}_{output\ c, fuel} = \mathbf{Fuel\ consumption}_{fuel} * \mathbf{EF}_{output\ c, fuel} \quad (4.3)$$

Where:

|  |  |
|--|--|
| $\mathbf{Emissions}_{output\ c, fuel}$ | = emissions of each output (e.g., CO <sub>2</sub> , CH <sub>4</sub> , etc.) during combustion by type fuel (kg).           |
| $\mathbf{Fuel\ consumption}_{fuel}$    | = amount of fuel combusted (e.g., kg, liters, MJ).   |
| $\mathbf{EF}_{output\ c, fuel}$        | = emission factor of an output during combustion by type of fuel (kg output/kg fuel, kg output/l fuel, kg output/MJ fuel). |

The total emissions of a particular output (e.g., CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O) is calculated following equation (4.4):

$$\mathbf{Emissions}_{output\ c} = \sum_{fuels} \mathbf{Emissions}_{output\ c, fuel} \quad (4.4)$$

Total emissions for each particular output due to pre-combustion and combustion of fuels used at each production phase of MK are calculated following equation (4.5):



$$Emissions_{output} = Emissions_{output\ pre-c} + Emissions_{output\ c} \quad (4.5)$$

#### 4.1.3.3 Electricity Generation LCI

Electricity generation LCI data was compiled from different sources in literature and required extensive calculations. Computation of U.S. total LCI emission factors was done based on the methodology followed by Gursel [110] and using the most recent data published by the Energy Information Administration (EIA) [113, 118, 119] and the “Emissions and Generation Resource Integrated Database” eGRID (2016) developed by the Environmental Protection Agency (EPA) [111].

##### i. Indirect Emissions from Electricity Generation in the United States.:

Computation of upstream emissions due to electricity generation are calculated based on methodology followed by Gursel [110] and considering the contribution of each energy source in the total electricity grid mix of each state within the U.S. Calculations of the electricity grid mix by energy source per state is shown in equation (4.6):

$$Grid\ mix\ \%_{state\ i,\ source\ k} = \frac{Energy\ generation_{state\ i,\ source\ k}}{Total\ energy\ generation_{state\ i}} \quad (4.6)$$

Where:

|  |  |
|--|--|
| Grid mix % <sub>state i, source k</sub>        | = percentage of energy source (e.g., coal, natural gas, nuclear, etc.) in state i used for electricity generation.         |
| Energy generation <sub>source k, state i</sub> | = energy generation by energy source (e.g., coal, natural gas, nuclear, etc.) in state i for electricity generation (kWh). |
| Total energy generation <sub>state i</sub>     | = total energy generation in state i associated to electricity generation (kWh).   |

Values of energy use, water, solid waste, and air emissions such as CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, CO<sub>2</sub>-eq, NO<sub>x</sub>, and SO<sub>2</sub> Sb, As, Be, Cd, CO, Cr, Co, Cu, CH<sub>2</sub>O, Pb, Mn, Hg, Ni, NMVOC, PM<sub>10</sub>, PM<sub>total</sub>, Se, VOC (unspecified) and Zn are adapted from Gursel [110] and their emissions in each state are calculated following equation (4.7):

$$EF_{upstream, state i} = \sum_{output} (Grid\ mix\ \%_{state\ i, source\ k}) * (Up.EF_{source\ k, output\ j}) \quad (4.7)$$

Where:

|                                       |   |
|---------------------------------------|---|
| $EF_{upstream, state i}$              | = calculated upstream emission factors in state i used for electricity generation (MJ/kWh or kg/kWh).                         |
| $Grid\ mix\ \%_{state\ i, source\ k}$ | = percentage of energy source (e.g., coal, natural gas, nuclear, etc.) in state i used for electricity generation.            |
| $Up.EF_{source\ k, output\ j}$        | = upstream emission factors associated with an energy source k used for electricity generation in state i (MJ/kWh or kg/kWh). |

## ii. Direct Emissions from Electricity Generation in the U.S.:

Computation of energy generation and use by state was performed following the step-by-step calculations explained in equations (4.8) - (4.13). Firstly, in each state, the fuel heat content by energy source for electricity generation is calculated as shown in equation (4.8):

$$Fuel\ heat\ content_{source\ k} = \frac{Energy\ generation_{source\ k}}{Energy\ consumption_{source\ k}} \quad (4.8)$$

Where:

|                                   |  |
|-----------------------------------|--|
| $Fuel\ heat\ content_{source\ k}$ | = amount of energy per unit of mass or volume generated by energy source (e.g., coal, natural gas, nuclear, etc.) in state i for electricity generation (MJ/kg, MJ/m <sup>3</sup> , MJ/l, MJ/kWh). |
| $Energy\ generation_{source\ k}$  | = energy generation by energy source (e.g., coal, natural gas, nuclear, etc.) in state i for electricity generation (kWh).   |
| $Energy\ consumption_{source\ k}$ | = consumption factor by energy source (e.g., coal, natural gas, nuclear, etc.) in state i for electricity generation (kg, m <sup>3</sup> , l, kWh).  |

With equation (4.20), the heat content of each energy source by state is calculated as shown in equation (4.9):

$$\mathbf{State\ fuel\ heat\ content} = \mathbf{Energy\ source}_{CF} * \mathbf{Fuel\ heat\ content}_{source\ k} \quad (4.9)$$

Where:

**State fuel heat content** = amount of energy generated by energy source (e.g., coal, natural gas, nuclear, etc.) in state i for electricity generation (MJ/kWh).

**Energy source<sub>CF</sub>** = consumption factor by energy source (e.g., coal, natural gas, nuclear, etc.) in state i for electricity generation (kg/kWh, m<sup>3</sup>/kWh, l/kWh, kWh/kWh).

**Fuel heat content<sub>source k</sub>** = amount of energy per unit of mass or volume generated by energy source (e.g., coal, natural gas, nuclear, etc.) in state i for electricity generation (MJ/kg, MJ/m<sup>3</sup>, MJ/l, MJ/kWh).

The direct embodied energy per kWh of electricity produced in each state is calculated as shown in equation (4.10):

$$\mathbf{EF}_{energy, direct} = \sum_{source} \mathbf{State\ fuel\ heat\ content} \quad (4.10)$$

Where:

**EF<sub>energy, direct</sub>** = direct energy generation in state i (MJ/kWh).

**State fuel heat content** = amount of energy generated by energy source (e.g., coal, natural gas, nuclear, etc.) in state i for electricity generation (MJ/kWh).

Finally, the total energy factor associated with electricity generation in the U.S. by state are calculated following equation (4.11):

$$\mathbf{EF}_{energy, state\ i} = \mathbf{EF}_{energy, upstream} + \mathbf{EF}_{energy, direct} \quad (4.11)$$

Air emissions such as CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, CO<sub>2</sub>-eq, NO<sub>x</sub>, and SO<sub>2</sub> were adopted from the “Emissions and Generation Resource Integrated Database” eGRID (2016) developed by the Environmental Protection Agency (EPA) [111]. Water use, solid waste and other air emissions such as Sb, As, Be, Cd, CO, Cr, Co, Cu, CH<sub>2</sub>O, Pb, Mn, Hg, Ni, NMVOC, PM<sub>10</sub>, PM<sub>total</sub>, Se, VOC (unspecified) and Zn are adapted from Gursel [110]. Total emissions for each particular output due to indirect and direct electricity generation in the U.S. by state are calculated following equation (4.12):

$$EF_{output, state i} = EF_{output, upstream} + EF_{output, direct} \quad (4.12)$$

Finally, the total emissions of a particular output (e.g., CO<sub>2</sub>, CH<sub>4</sub>, etc.) associated with electricity generation (both upstream and direct emissions) used at each production phase of MK is calculated following equation (4.13):

$$Emissions_{output, electricity} = Electricity\ consumption * EF_{output, state i} \quad (4.13)$$

Where:

- |  |   |
|--|---|
| Emissions <sub>output, electricity</sub> | = emissions of each output (e.g., CO <sub>2</sub> , CH <sub>4</sub> , etc.) associated with electricity generation. |
| Electricity consumption                  | = amount of electricity used at each production phase (kWh).  |
| EF <sub>output, state i</sub>            | = emission factor of an output associated with electricity generation (kg output/kWh).                              |

Table 4.2 summarizes the data collected with their respective sources to build the life-cycle inventory data on emissions associated to electricity generation in the U.S. Data cited in Table 4.2 are available in the MKC-LCA Tool and in the Appendix section of this dissertation. These tables were created following step-by-step calculations according to the equations (4.8) - (4.13).

**Table 4.2** - Summary of U.S. electricity generation LCI data. Tables and calculations are detailed in the MKC-LCA Tool and in the Appendix section.

| <b>Table ID</b> | <b>Description</b>   | <b>Reference</b>   |
|-----------------|--|--|
| LCI_06          | Electric Power Sector Consumption Estimates (MJ).  | EIA, State Energy Data System (SEDS), State Energy Consumption Estimates 2016 [113].                   |
| LCI_07          | Net Electric Power Sector Generation (kWh), 2016.  | EIA, State Energy Data System (SEDS), Annual Generation State 2016 [118].                              |
| LCI_08          | Electricity grid mix percentages by state.   | Calculated from Table LCI_07   |
| LCI_09          | Electric Power Sector Consumption Estimates (physical units), 2016.  | EIA, State Energy Data System (SEDS) [119].  |
| LCI_10          | Energy source consumption factor per kWh hour of electricity.  | Calculated with Table LCI_07 and Table LCI_09  |
| LCI_11          | Fuel heat content values for Electric Power Generation.  | Calculated with Table LCI_06 and Table LCI_09  |
| LCI_12          | State Fuel Heat Content Conversion Factors (MJ/kWh), 2016.   | Calculated by multiplication of factors in Table LCI_10 and Table LCI_11.                              |
| LCI_13          | Direct LCI emission factors of GHG, Nox, and SO <sub>2</sub> by U.S. State.  | eGRID 2016 [111].  |
| LCI_14          | Direct Emissions for LCI Data for Electricity Grid Mix by States and U.S. Average (unit/kWh electricity)                                     | Calculated by multiplication and summation of factors in Table LCI_03, Table LCI_08, and Table LCI_13. |
| LCI_15          | Upstream Emissions for LCI Data for Electricity Grid Mix by States and U.S. Average (unit/kWh electricity)                                   | Calculated from Table LCI_05 and Table LCI_08.   |
| LCI_16          | Total Emissions for LCI Data for Electricity Grid Mix by States and U.S. Average (unit/kWh electricity). Table A. 6 in the Appendix section. | Calculated from Table LCI_14 and Table LCI_15.   |

### iii. Emissions from Electricity Generation for User-specific Grid Mix:

The MKC-LCA Tool allows the user to define up to three custom electricity grids to calculate the environmental impact of metakaolin production in any region of the world as long as the percentages of energy sources for electricity generation are known. When the electricity grid mix is defined by the user (i.e., modeling parameters for electricity outside the 50 U.S. States), emission factors collected from U.S. and international databases were compiled by Gursel [110] and adapted for this study in Table A. 4 and Table A. 5 in the Appendix section. With these data, Table *LCI\_17 Direct Emissions for LCI Data for User-specific Electricity Grid Mix* (unit/kWh electricity) and

Table *LCI\_18 Total Emissions for LCI Data for User-specific Electricity Grid Mix* (unit/kWh electricity) were calculated. Step-by-step calculations in the MKC-LCA Tool are detailed as shown in equations (4.14) - (4.17). Indirect emission factors associated with electricity generation are calculated following equation (4.14):

$$EF_{output, upstream} = \sum_{output} (user - specific\ grid\ mix\ \%_{source\ k}) * (Up.EF_{source\ k, output\ j}) \quad (4.14)$$

Where:

|  |  |
|--|--|
| $EF_{output, upstream}$                    | = calculated upstream emission factors associated with electricity generation for a user-specific grid mix (MJ/kWh or kg/kWh).                         |
| User-specific grid mix<br>$\%_{source\ k}$ | = percentage of energy source (e.g., coal, natural gas, nuclear, etc.) used for electricity generation according to the user-specific grid mix inputs. |
| $Up.EF_{source\ k, output\ j}$             | = upstream emission factors associated with an energy source k used for electricity generation (MJ/kWh or kg/kWh).                                     |

Direct emission factors associated with electricity generation are calculated following equation (4.15):

$$EF_{output, direct} = \sum_{output} (user - specific\ grid\ mix\ \%_{source\ k}) * (EF_{source\ k, output\ j}) \quad (4.15)$$

Where:

|  |  |
|--|--|
| $EF_{output, direct}$                      | = Calculated direct emission factors associated with electricity generation for a user-specific grid mix (MJ/kWh or kg/kWh).                           |
| User-specific grid mix<br>$\%_{source\ k}$ | = percentage of energy source (e.g., coal, natural gas, nuclear, etc.) used for electricity generation according to the user-specific grid mix inputs. |

$EF_{\text{source } k, \text{ output } j}$  = direct emission factors associated with an energy source  $k$  used for electricity generation (MJ/kWh or kg/kWh).

Total emissions for each particular output due to indirect and direct electricity generation for a user-specified grid mix are calculated following equation (4.16):

$$EF_{\text{output}} = EF_{\text{output, upstream}} + EF_{\text{output, direct}} \quad (4.16)$$

Finally, the total emissions of a particular output (e.g., CO<sub>2</sub>, CH<sub>4</sub>, etc.) associated with electricity generation (both upstream and direct emissions) for a user-specific grid mix used at each production phase of MK is calculated following equation (4.17):

$$Emissions_{\text{output, electricity}} = Electricity\ consumption * EF_{\text{output}} \quad (4.17)$$

Where:

$Emissions_{\text{output, electricity}}$  = emissions of each output (e.g., CO<sub>2</sub>, CH<sub>4</sub>, etc.) associated with electricity generation.

Electricity consumption = amount of electricity used at each production phase (kWh).

$EF_{\text{output}}$  = emission factor of an output associated with electricity generation (kg output/kWh) for a user-specific grid mix.

#### 4.1.3.4 Transportation LCI

When available, tail-pipe impacts and indirect impacts from the supply chain of freight transportation were included in the calculations of emissions associated with the transportation of raw materials and finished products to and from the metakaolin or cement plant. Different modes of transportation (e.g., road and rail freight vehicles, and water transportation) are available in the tool for the user to consider their contribution to the environmental assessment.

Hybrid LCA of freight transportation in the U.S. has been carefully detailed by Facanha and Horvath [115]. Emissions factors provided by these authors were calculated based on 2005 vehicle models. Because of the longer service life of freight vehicles typically used in the U.S. [120], values from this study are still relevant and applied to the most common vehicles likely still in use in the cement and concrete industry. New technologies on fuel efficiency of freight vehicles evolve at a slower rate than those associated with passenger vehicles, suggesting that GHG emissions from freight transportation would decrease at a slower rate than those from passenger

transportation. Thus, these air emission factors are still relevant to time of publication of this dissertation. Due to scarcity of comparable studies on complete life-cycle assessment of emissions associated with vehicles and transportation before and beyond the vehicles' operational phase (i.e., tailpipe emissions) [115, 120], MKC-LCA Tool only considers emissions associated with vehicle technology corresponding to freight transportation within the U.S. (Table 4.3). Future additions to the tool will contain life-cycle emission factors for transportation modes and vehicles outside the continental U.S. when these data become available in literature.

**Table 4.3** – Transportation life-cycle emissions inventory. Table ID: LCI\_Transportation\_01

|                     | Unit | Truck class 8b (Model 2005) | Truck class 5 (Model 2005) | Truck class 2b (Model 2005) | Rail (4,000 hp diesel-electric locomotives) | Water (International container) |
|---------------------|------|-----------------------------|----------------------------|-----------------------------|---|---------------------------------|
| <b>Unit</b>         |      | <b>kg-km</b>                | <b>kg-km</b>               | <b>kg-km</b>                | <b>kg-km</b>                                | <b>kg-km</b>                    |
| Energy              | MJ   |                             |                            |                             |   | 2.49E-04                        |
| CO <sub>2</sub> -eq | kg   | 1.28E-04                    | 1.58E-04                   | 1.98E-04                    | 2.74E-05                                    | 1.40E-05                        |
| CO <sub>2</sub>     | kg   | 1.28E-04                    | 1.58E-04                   | 1.98E-04                    | 2.74E-05                                    | NS                              |
| CO                  | kg   | 4.11E-07                    | 8.22E-07                   | 1.26E-06                    | 2.88E-07                                    | NS                              |
| NO <sub>x</sub>     | kg   | 1.76E-06                    | 1.12E-06                   | 1.21E-06                    | 5.07E-07                                    | NS                              |
| PM <sub>10</sub>    | kg   | 2.40E-07                    | 3.22E-07                   | 4.04E-07                    | 3.42E-08                                    | NS                              |
| SO <sub>2</sub>     | kg   | 1.03E-07                    | 2.05E-07                   | 3.08E-07                    | 8.22E-08                                    | NS                              |
| Reference           |      | [115]                       | [115]                      | [115]                       | [115]                                       | [116]                           |

\*NS = Not specified

For the calculation of energy and air emissions associated to transportation of materials throughout the system boundary (i.e., cradle to gate), the modes of transportation and the distances traveled per each segment of the route (i.e., in the case of multimodal transportation) are collected from *The User Input* sheet and multiplied by each emission factor from the *Transportation* sheet (Table 4.3) as shown in equation (4.18):

$$Emissions_{unit\ of\ material,j} = \sum_{modes} (Distance_{traveled,mode\ i} \times EF_{mode\ i}) \quad (4.18)$$



Where:

|                                      |  |
|--------------------------------------|--|
| $Emissions_{unit\ of\ material,\ j}$ | = emissions of each output (e.g., CO <sub>2</sub> , CH <sub>4</sub> ) in MJ or kg per unit of mass of material transported in transportation scenario j. |
| $Distance_{traveled,\ mode\ i}$      | = distance traveled in km by transportation mode i.  |
| $EF_{mode,\ i}$                      | = emission factor of an output during transportation by mode i (MJ or kg output/kg-km).  |

Results from equation (4.18) are expressed per unit of mass of material transported, these values are then multiplied by the total mass of material that is being transported in each transportation scenario in order to calculate the total amount of emissions associated with that transportation scenario as shown in equation (4.19):

$$Emissions_{transportation,\ j} = Emissions_{unit\ of\ material,\ j} \times Mass_{material} \quad (4.19)$$

Where:

|                                      |  |
|--------------------------------------|--|
| $Emissions_{transportation,\ j}$     | = emissions of each output (e.g., CO <sub>2</sub> , CH <sub>4</sub> ) in MJ or kg per total mass of material transported in transportation scenario j.   |
| $Emissions_{unit\ of\ material,\ j}$ | = emissions of each output (e.g., CO <sub>2</sub> , CH <sub>4</sub> ) in MJ or kg per unit of mass of material transported in transportation scenario j. |
| $Mass_{material}$                    | = mass of material transported in kg.  |

Finally, the total energy used or emissions of a particular output (e.g., CO<sub>2</sub>, CH<sub>4</sub>, etc.) is calculated following equation (4.20):

$$Emissions_{transportation,\ k} = \sum_{Transportation\ inputs} (Emissions_{transportation,\ j}) \quad (4.20)$$

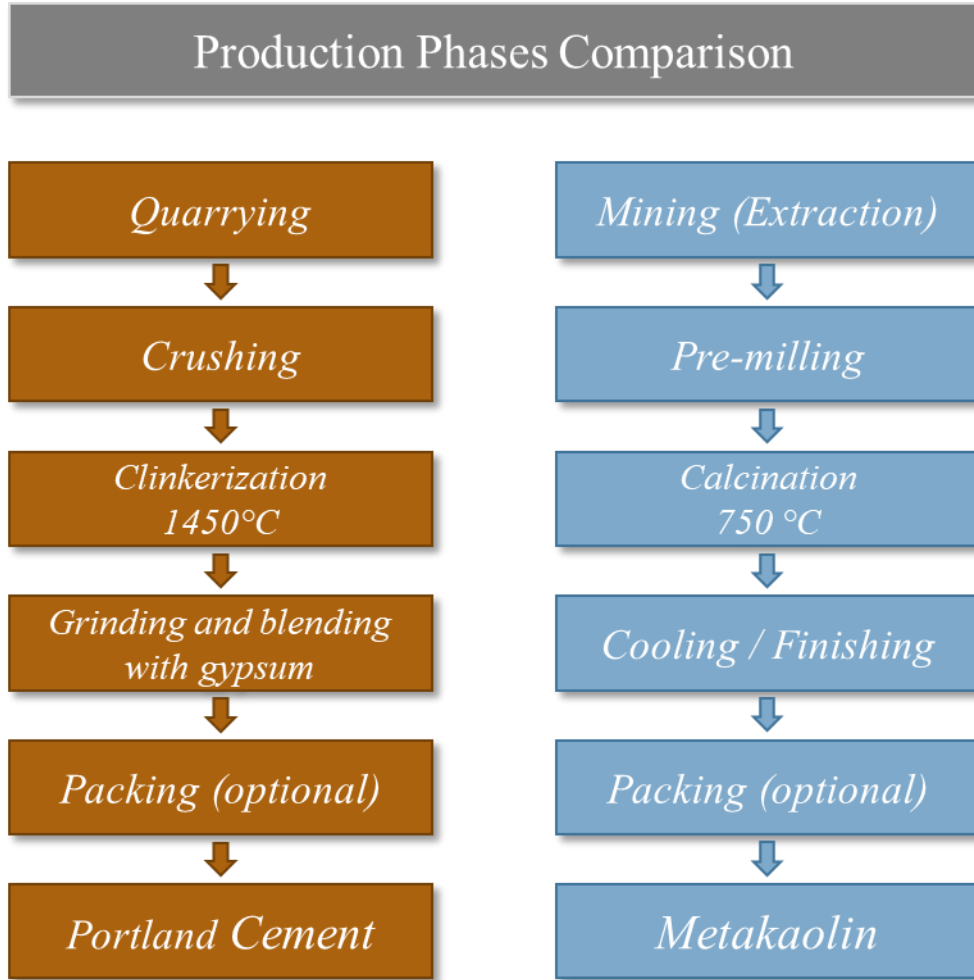
Where:

Emissions<sub>transportation, k</sub> = Total emissions of each output k (e.g., CO<sub>2</sub>, CH<sub>4</sub>) in MJ or kg associated with the transportation of material within the system boundary.

Emissions<sub>transportation, j</sub> = emissions of each output (e.g., CO<sub>2</sub>, CH<sub>4</sub>) in MJ or kg per total mass of material transported in transportation scenario j.

#### 4.1.4 Production Phases

Metakaolin is the final product from the calcination of clay rich in kaolin mineral. Production of metakaolin is similar to that of cement manufacturing. First, the raw clay is mined and brought to the plant where processing and calcination take place. Figure 4.10 shows a comparison of each stage of processing of cement and metakaolin.



**Figure 4.10** - Comparison of production phases in cement and metakaolin manufacturing.

User input data is entered in the tool in order to account for all the energy and resources used during each of the production phases for metakaolin production which in turn are multiplied for each emission factor detailed in the Life-Cycle Inventories section 4.1.3. With the aim of building the *Phases Inventories* sheets, data reported in literature were complemented with data values collected from different companies and researchers through a confidential life-cycle inventory survey that encompassed the following questions (See Table 4.4)

**Table 4.4** – Life-cycle inventory survey distributed to companies and researchers.

| <b>Code</b>                       | <b>Question</b>   |
|-----------------------------------|---|
| <b>Raw Materials</b>              |   |
| Q.1                               | What is the amount of raw clay required to produce 1 kg of metakaolin?  |
| Q.2                               | What is the average grade (purity) of the kaolinitic clays?   |
| Q.3                               | What is the average size of the clays before calcination?   |
| Q.4                               | What is the average size of the clays after calcination and/or the finished metakaolin?   |
| Q.5                               | What is the fuel mix used for the calcination process?  |
| <b>Extraction Phase</b>           |   |
| Q.6                               | Where is the source of clays (i.e., deposit, mine, quarry) located?   |
| Q.7                               | What is the extraction process?   |
| Q.8                               | What inputs (e.g., materials, fuels, equipment) are needed during the extraction phase?   |
| Q.9                               | What is the transportation mode used to transport the raw materials from the clay deposits to the production plant?                   |
| <b>Production Phase</b>           |   |
| Q.10                              | What is the production scheme for calcined clay (e.g., extraction, calcination, mixing, grinding, packing)?                           |
| Q.12                              | What is the grinding technology used, if any?   |
| Q.13                              | What is the temperature of calcination of your material? Do you use different calcination temperatures with different types of clays? |
| Q.14                              | What is the clay calcining technology currently used at industrial scale?   |
| Q.15                              | What inputs (e.g., materials, fuels, equipment) are needed during each production phase?  |
| Q.16                              | What is the production capacity of the metakaolin plant (e.g., tonne/day or tonne/year)?  |
| Q.17                              | If cement and metakaolin are both processed at the same plant, do you use separate production lines for each product?                 |
| Q.18                              | Does the grinding process of metakaolin and cement before blending occur separately or by means of co-grinding in the same equipment? |
| Q.19                              | What are the distances traveled at each stage of the production of metakaolin?  |
| <b>Particulate Matter Control</b> |   |
| Q.20                              | Does the plant have any system in place to measure and control particulate matter emissions?  |
| Q.21                              | Does the plant have any system in place to measure and control solid waste?   |
| <b>Final Product</b>              |   |
| Q.22                              | What are the percentages of replacement of cement by metakaolin and limestone in your final products?                                 |
| Q.23                              | What is the commercial name of your final product?  |
| Q.24                              | What is the commercial cost of your final product?  |
| Q.25                              | Who is the target market for your final product?  |

#### **4.1.4.1 Raw Material Extraction**

The mining process for kaolin clay is commonly done by means of open pit extraction as it is done in BASF's mines located in Middle Georgia (GA) [121]. First the overburden is removed (typically from several feet up to several tens feet deep) followed by mining of the kaolin layer. Once the kaolin extraction is completed, the mine is closed down and the open pit area is reclaimed [121]. Other extraction technique reported in literature is hydraulic mining which was commonly done in the U.K. and it is known for producing large quantities of sediments in water bodies [70]. Unfortunately, no data on inventory of resources and energy used during extraction by means of hydraulic mining was found. However, the tool has a placeholder for inserting LCI data for this method in the future.

As reported from industrial trials, the extraction of the raw kaolin clay is usually done by means of open pit extraction using 20- or 22-tonne hydraulic excavators. The material is then loaded onto heavy duty trucks using front-end loaders [122]. It is considered that the deposits and quarrying sites of raw kaolin are located in close proximity to the metakaolin or cement production plant (less 30 kms of distance between locations). The MCK-LCA Tool includes energy use (electricity and fuels) as well as water consumption values for kaolin extraction. These values were adopted from those reported by Gursel [110] based on data from the National Renewable Energy Laboratory (NREL) for open pit extraction of limestone for cement production [123] and are detailed in Table 4.5. It is worth nothing that this is a conservative estimation due to kaolin clay's softness in comparison with limestone. Similar to limestone quarrying process for clinker production, water consumption during the mining of raw clays is mainly used for the suppression of dust in the roads during transportation of raw materials from the quarry to the production facility [124]. Particulate-matter is the primary process-related air pollutant during mining and extraction of the clays which comprises crushing, screening, and transportation of the raw material.

**Table 4.5** - Energy use, water consumption and PM emissions from open pit extraction of kaolin. Adapted from [110] based on [123]. Table ID: LCI\_Ext\_01

| <b>Inputs</b>                     | <b>(Per tonne of raw kaolin)</b> | <b>Unit</b>    |
|-----------------------------------|----------------------------------|----------------|
| Bituminous coal                   | 0.036                            | kg             |
| Natural gas                       | 0.140                            | m <sup>3</sup> |
| Distillate (Diesel) fuel oil      | 0.584                            | l              |
| Gasoline                          | 0.051                            | l              |
| Electricity                       | 4.230                            | kWh            |
| Water                             | 4.351                            | m <sup>3</sup> |
| <b>Process-related emissions:</b> |                                  |                |
| PM <sub>10</sub>                  | 0.0511                           | kg             |

Total energy and water use, as well as LCI emissions associated with raw kaolin clay extraction are computed based on *The User Input* selection sheet, the LCI data collected in Table 4.5. Firstly, total electricity use for raw kaolin clay extraction is calculated following equation (4.29):

$$Electricity_{total, extraction} = Electricity_{extraction} * \frac{1}{1000} * Raw\_Clay \quad (4.21)$$

Where:

Electricity<sub>total, extraction</sub> = amount of electricity used for the extraction of raw kaolin clay (kWh).

Electricity<sub>extraction</sub> = amount of electricity used for the extraction of one tonne of raw kaolin clay (kWh/tonne of raw clay).

Raw\_Clay = amount of raw clay modeled (kg). Corresponds to 1.185 times the FU modeled by the user.

In order to calculate the emissions associated with fuel combustion and pre-combustion from fuel consumption during raw clay extraction, the total fuel consumption needed for raw clay extraction is first calculated following equation (4.30), data from Table 4.5, and *The User Input* selection on the amount of metakaolin modeled:

$$\begin{aligned}
 & \text{Fuel consumption}_{\text{total extraction, fuel } j} \\
 & = \text{Fuel consumption}_{\text{extraction, fuel } j} * \frac{1}{1000} * \text{Raw\_Clay}
 \end{aligned}
 \tag{4.22}$$

Where:

|  |  |
|--|--|
| Fuel consumption <sub>total extraction, fuel j</sub> | = amount of fuel j used for the extraction of raw kaolin clay (e.g., kg, liters, m <sup>3</sup> ).   |
| Fuel consumption <sub>extraction, fuel j</sub>       | = amount of fuel j used for the extraction of one tonne of raw kaolin clay (kg/tonne of raw clay, l/ tonne of raw clay, m <sup>3</sup> / tonne of raw clay). |
| Raw_Clay   | = amount of raw clay modeled (kg). Corresponds to 1.185 times the FU modeled by the user.  |

Finally, the total energy, water use, and emissions of a particular output (e.g., CO<sub>2</sub>, CH<sub>4</sub>, etc.) associated with the total electricity use during extraction of the raw clay are calculated using the LCI factors from electricity generation (both upstream and direct emissions) described in Section 4.1.3.3 for the electricity grid mix used at the mining site where extraction of the raw clay takes place. LCI factors from electricity generation are then multiplied by the total electricity use during extraction from equation (4.21) as shown in equation (4.23) below:

$$\text{Emissions}_{\text{output, electricity-extraction}} = \text{Electricity}_{\text{total, extraction}} * \text{EF}_{\text{output}}
 \tag{4.23}$$

Where:

|   |   |
|---|---|
| Emissions <sub>output, electricity-extraction</sub> | = emissions of each output (e.g., CO <sub>2</sub> , CH <sub>4</sub> , etc.) associated with electricity consumption during extraction phase (kg). |
| Electricity <sub>total, extraction</sub>            | = amount of electricity used for the extraction of raw kaolin clay (kWh).   |
| EF <sub>output</sub>                                | = emission factor of an output associated with electricity generation (kg output/kWh).  |

Lastly, the total energy, water use, and emissions of a particular output (e.g., CO<sub>2</sub>, CH<sub>4</sub>, etc.) associated with the fuels used during extraction of the raw clay are calculated using the LCI factors from fuel pre-combustion and fuel combustion described in Section 4.1.3.1 and Section

4.1.3.2. Fuels LCI factors are then multiplied by the total fuel consumption of each fuel from equation (4.22) as shown in equation (4.24) below:

$$\mathbf{Emissions}_{output, fuel\ j-extraction} = \mathbf{Fuel\ consumption}_{total\ extraction, fuel\ j} * \mathbf{EF}_{output} \text{ (eq. 4.5)} \quad (4.24)$$

Where:

|   |   |
|---|---|
| $\mathbf{Emissions}_{output, fuel\ j-extraction}$         | = emissions of each output (e.g., CO <sub>2</sub> , CH <sub>4</sub> , etc.) associated with fuel j consumption during extraction phase (kg).  |
| $\mathbf{Fuel\ consumption}_{total\ extraction, fuel\ j}$ | = amount of fuel j used for the extraction of raw kaolin clay (e.g., kg, liters, m <sup>3</sup> ).  |
| $\mathbf{EF}_{output}$                                    | = emission factor of an output associated with fuel j pre-combustion and combustion (kg output/kg fuel j, kg output/l fuel j, kg output/m <sup>3</sup> fuel j) as calculated in equation (4.5). |

Additionally, particulate matter emissions as well as direct water consumption from the raw clay extraction process are calculated and following equation (4.25):

$$\mathbf{Emissions}_{direct, extraction} = \mathbf{Raw\_Clay} * \mathbf{EF}_{output} * \frac{\mathbf{1}}{\mathbf{1000}} \quad (4.25)$$

Where:

|   |   |
|---|---|
| $\mathbf{Emissions}_{direct, extraction}$ | = emissions of each output (i.e., PM <sub>10</sub> , and water) associated with raw clay extraction phase (kg, m <sup>3</sup> ).  |
| $\mathbf{Raw\_Clay}$                      | = amount of raw clay modeled (kg). Corresponds to 1.185 times the FU modeled by the user.   |
| $\mathbf{EF}_{output}$                    | = emission factor of an output (i.e., PM <sub>10</sub> , and water) associated with raw clay extraction phase (kg PM <sub>10</sub> /tonne of raw clay, m <sup>3</sup> water/tonne of raw clay). |



#### 4.1.4.2 Transportation

Metakaolin processing requires the transportation of raw materials and finished products within the system boundary (i.e., cradle to gate). Five transportation modes commonly used in the cement and concrete industry are available in the tool (i.e., Truck class 8b, truck class 5, truck class 2b, rail and water containers) in *The User Input* sheet (Section 4.1.2.7) and the *Transportation* sheet contains their associated life-cycle inventory of energy use and emission factors (Section 4.1.3.4).

#### 4.1.4.3 Raw Material Drying and Pre-milling

After mining, the raw material is brought to the production plant to be processed into metakaolin. When moisture content is high (higher than 20%), preparation before calcination involves drying the calciner feed material (hydrous kaolin clay) and pulverizing it with conventional milling equipment [125]. Values of energy and resources used during the clay pre-milling phase were adapted from those reported for raw meal grinding for portland cement production. It is worth noting that this is a conservative estimation due to kaolin clay's softness in comparison with cement raw materials. Since crushing and grinding of the raw material typically occur in dry conditions, no water is required for the equipment listed in Table 4.6. An additional advantage when using vertical roller mills for the grinding phase is that drying of the raw clays could also be performed with moisture contents of up to 20% [126, 127].

Drying of supplementary cementitious materials such as kaolin clays could be required and the thermal heat input could be extracted from the kiln exhaust gases or from the cooling exhaust gases during the cooling phase [128]. In certain cases, heating and drying of the raw clay occurs during the first stage of the calcination process when a rotary kiln with cyclones preheaters and/or precalciner are used for the calcination phase or during the first stage of calcination using a flash calciner [129]

**Table 4.6** - Electricity use for metakaolin pre-milling technology options. Table ID: LCI\_PreMill\_01a

| Grinding Technology               | Electricity (kWh/tonne of raw clay) |      |         |           |
|-----------------------------------|-------------------------------------|------|---------|-----------|
|                                   | Min                                 | Max  | Average | Reference |
| Ball Mill_Dry grinding            | 15.6                                | 17   | 16.3    | [128]     |
| Tube Mill_Dry grinding            | 18.5                                | 18.5 | 18.5    | [110]     |
| Vertical Roller Mill_Dry grinding | 13                                  | 14   | 13.5    | [128]     |
| No_Pre-grinding                   | 0                                   | 0    | 0       |           |

Particulate matter (PM) is the main process-based emissions from pre-milling of metakaolin. Due to the lack of primary data on air emissions from metakaolin pre-milling and handling at industrial scale, the tool has adopted particulate matter emissions associated with cement raw meal pre-milling. To control the release of PM to the environment, fabric filters for dust control in the pre-milling systems are included in the MKC-Tool. The U.S. EPA Compilation of Air Pollutant Emission Factors AP-42 is adapted to calculate the total PM emissions ( $PM_{Total}$ )

associated with metakaolin pre-milling [124]. Table 4.7 shows the electricity use and PM emissions of these filters by tonne of raw clay.

**Table 4.7** - Electricity use and PM emissions for PM control technology during metakaolin pre-milling. Table ID: LCI\_PreMill\_01b

| Technology         | PM Emission Control Technology Option   |       |            |                                |       |         |
|--------------------|---|-------|------------|--------------------------------|-------|---------|
|                    | Electricity use (kWh/tonne of raw clay) |       |            | PMtotal (kg/tonne of raw clay) |       |         |
|                    | Min                                     | Max   | Average    | Min                            | Max   | Average |
| Fabric Filter (FF) | 0.4                                     | 0.6   | 0.5        | 0.028                          | 0.040 | 0.034   |
| Reference          | [128]                                   | [128] | Calculated | [130]                          | [130] | [130]   |

Calculations of total electricity includes the electricity consumption of the pre-milling technology option selected by the user and the added electricity consumption of the PM control technology collected from *The User Input* sheet and multiplied by the electricity consumption factors found in the *Pre-milling* sheet (Table 4.6 and Table 4.7) as shown in equation (4.26). It is worth noting that the total value of electricity use is during pre-milling is calculated with the total amount of raw clay (instead of metakaolin) modeled. The amount of raw clay modeled is automatically calculated by the tool based on the average ratio of raw clay to finished metakaolin (1.185:1) reported in literature from several industrial trials [71, 122].

$$\begin{aligned}
 & \mathbf{Electricity}_{total, \text{ pre-milling}} \\
 & = (\mathbf{Electricity}_{\text{pre-milling option } i} + \mathbf{Electricity}_{\text{PM control option } k}) * \frac{1}{1000} * \mathbf{Raw\_Clay} \quad (4.26)
 \end{aligned}$$

Where:

$\mathbf{Electricity}_{total, \text{ pre-milling}}$  = amount of electricity used for the pre-milling technology option i, including the electricity use of the PM control technology option k (kWh).

$\mathbf{Electricity}_{\text{pre-milling option } i}$  = amount of electricity used for the pre-milling technology option i (kWh/tonne of raw clay).

$\mathbf{Electricity}_{\text{PM control option } k}$  = amount of electricity used for the PM control technology option k (kWh/tonne of raw clay).

$\mathbf{Raw\_Clay}$  = amount of raw clay modeled (kg). Corresponds to 1.185 times the FU modeled by the user.

Subsequently, the energy use and total emissions of a particular output (e.g., CO<sub>2</sub>, CH<sub>4</sub>, etc.) associated with electricity consumption during raw clay pre-milling are calculated following equation (4.35):

$$\mathbf{Emissions}_{output, pre-milling} = \mathbf{Electricity}_{total, pre-milling} * \mathbf{EF}_{output} \quad (4.27)$$

Where:

|                                    |  |
|------------------------------------|--|
| $Emissions_{output, pre-milling}$  | = emissions of each output (e.g., CO <sub>2</sub> , CH <sub>4</sub> , etc.) associated with electricity consumption during pre-milling phase (kg). |
| $Electricity_{total, pre-milling}$ | = amount of electricity used for the pre-milling technology option i, including the electricity use of the PM control technology option k (kWh).   |
| $EF_{output}$                      | = emission factor of an output associated with electricity generation (kg output/kWh).   |

Additionally, particulate matter emissions from the raw clay pre-milling process are calculated based on inventory data reported in Table 4.7 and following equation (4.36):

$$\mathbf{Emissions}_{direct, grinding} = \mathbf{FU} * \mathbf{EF}_{output} * \frac{\mathbf{1}}{\mathbf{1000}} \quad (4.28)$$

Where:

|                                |  |
|--------------------------------|--|
| $Emissions_{direct, grinding}$ | = emissions of each output (i.e., PM, PM <sub>10</sub> , and water) associated with metakaolin grinding phase (kg).                                |
| $FU$                           | = functional unit modeled (kg of metakaolin).  |
| $EF_{output}$                  | = emission factor of an output (i.e., PM, PM <sub>10</sub> , and water) associated with metakaolin grinding phase (kg output/tonne of metakaolin). |

#### 4.1.4.4 Raw Material Calcination

Calcination is the most important phase during metakaolin production. In order to produce a reactive and pozzolanic material, clay rich in kaolin has to be fired to temperatures between 750°C and 800°C for 30 to 45 minutes and up to two hours depending on the equipment and the clay being calcined [121, 122]. At industrial scale, it has been demonstrated that calcination of kaolin clay does not require high investment costs in new equipment since it can be calcined using existing calcination system for clinker production [84]. Technology options and their thermal energy consumption were collected from an online survey distributed to the main metakaolin producers and one cement company in the U.S., insights reported from industrial trials, and peer-reviewed literature. For metakaolin calcination using an idle wet rotary kiln, thermal energy input of 4100 MJ/tonne of metakaolin has been reported by [23]. For dry rotary kilns, thermal energy input of 3235 and 2513 MK/tonne of metakaolin have been reported by [39] and [122] respectively. For flash calciners, thermal energy inputs of 2275 MJ/tonne of metakaolin reported by FLSmidth & Co., 1895 MJ/tonne of metakaolin reported by [23], and 2500 MJ/tonne of metakaolin reported by [70]. These values were adopted in the tool and are compiled in Table 4.8.

**Table 4.8** - Thermal energy consumption of different technology options for kaolin clay calcination.

| <b>Kaolin Calcination Technology Option</b> | <b>Unit (per tonne of metakaolin)</b> | <b>Thermal Energy Consumption</b> | <b>Reference</b> |
|---|---------------------------------------|-----------------------------------|------------------|
| Flash Calciner                              | MJ                                    | 2223.2                            | [23, 39, 70]     |
| Dry Rotary Kiln                             | MJ                                    | 2873.5                            | [122], [39]      |
| Wet Rotary Kiln                             | MJ                                    | 4100                              | [23, 71]         |

Additional LCI calculations related to the clay calcination process include the kiln electricity use and water input depending on the selected calcination technology. Table 4.9 contains data for electricity use during calcination adopted from industrial trials in Cuba, India, and Colombia. When not available, data reported by the Portland Cement Association (PCA) [124] for clinker kiln firing were considered as a conservative approach due to similarities in both processes.

**Table 4.9** - Electricity use, water consumption, process-related PM emissions by calcination technology. Table ID: LCI\_CAL\_02

| <b>Kaolin Calcination Technology Option</b> | <b>Electricity Use (kWh/ tonne of metakaolin)</b> | <b>Water (kg/ tonne of metakaolin)</b> | <b>Reference, Electricity</b> | <b>Reference, Water</b> |
|---|---|--|-------------------------------|-------------------------|
| <b>Flash Calciner</b>                       | 16.7  | 0                                      | [39]                          | [131]                   |
| <b>Dry Rotary Kiln</b>                      | 25.75   | 0                                      | [34], [122]                   | [122]                   |
| <b>Wet Rotary Kiln</b>                      | 39  | 485                                    | [34]                          | [124]                   |

The calcination process requires a source of energy to feed the calciner and allow for dihydroxylation of the raw kaolin clay. Conventional fuels used in kiln firing systems are bituminous coal, petroleum coke, (heavy) fuel oil, and natural gas. In order to reduce costs from fuel procurement, and to sustainably eliminate a variety of hazardous waste, alternative or waste fuels have been recently adopted [128]. Waste fuels included in the tool are waste oils, waste tires, waste paper, waste plastics, waste sewage sludge, and other wastes. As defined in Section 4.1.2.6, the user can define the fuel mix used for metakaolin calcination when these values are known. If the user does not know the fuel mix used for the calcination process, the U.S. average fuel mix input for clinker kiln firing (Table 4.10) is available to perform a complete assessment. Preparation of the fossil and waste fuels typically used for this phase of production includes milling (coal and petcoke), drying, shredding (in the case of waste tires), heating, and pumping (in the case of fuel oils and liquid waste fuels). Alternative or waste fuels are usually prepared by the supplier outside the cement or metakaolin plant [128]. Electricity use factors for the preparation of most common fuels used in the kiln were adapted from those reported by Gursel [110] and are summarized in Table 4.10.

**Table 4.10** - Electricity use factors for fuel preparation and U.S. average kiln fuel mix. Adapted from Gursel [110]. Table ID: LCI\_CAL\_03

| <b>Input Fuels</b>           | <b>(kWh/tonne of metakaolin)</b> | <b>U.S. Average Kiln Fuel Mix</b> |
|------------------------------|----------------------------------|-----------------------------------|
| Bituminous coal              | 40                               | 64.1%                             |
| Lignite coal                 | 35                               | 0%                                |
| Petroleum coke               | 45                               | 21.2%                             |
| Natural gas                  | 0                                | 3.7%                              |
| Residual (heavy) fuel oil    | 3                                | 0.2%                              |
| Distillate (Diesel) fuel oil | 0                                | 0.8%                              |
| Waste oil                    | 3                                | 0.3%                              |
| Waste solvent                | 3                                | 4.0%                              |

|                               |    |      |
|-------------------------------|----|------|
| Waste tire (whole)            | 3  | 1.8% |
| Waste tire (shredded)         | 45 | 1.8% |
| Waste paper (cardboard, wood) | 25 | 0%   |
| Waste plastics                | 43 | 0%   |
| Waste sewage sludge (dry)     | 8  | 0%   |
| Waste (other/non-hazardous)   | 25 | 2.1% |
| Waste (other/hazardous)       | 45 | 0%   |

Dust and particulate matter from kilns and calciners consist of raw kaolin clay particles that are suspended in the exhaust air. Because industrial trials of metakaolin calcination have been done at existing cement plants, PM control technologies often used in the kilns for clinker production are adopted in the MKC-Tool. The most common technologies are fabric filters (FF) and electrostatic precipitators (ESP). Table 4.11 contains the electricity factors and PM emissions associated with each technology which are used to calculate the overall electricity use and emissions associated with PM control during metakaolin calcination.

**Table 4.11** - Electricity use and PM emissions for PM control technology during metakaolin calcination. Table ID: LCI\_CAL\_04

| Technology                        | PM Emissions Control Technology Option    |       |            |                               |            |            |                                  |            |            |
|-----------------------------------|---|-------|------------|-------------------------------|------------|------------|----------------------------------|------------|------------|
|                                   | Electricity use (kWh/tonne of metakaolin) |       |            | PM10 (kg/tonne of metakaolin) |            |            | PMtotal (kg/tonne of metakaolin) |            |            |
|                                   | Min                                       | Max   | Average    | Min                           | Max        | Average    | Min                              | Max        | Average    |
| None                              | 0   | 0     | 0          | 170                           | 410        | 280        | 500                              | 630        | 550        |
| Fabric Filter (FF)                | 1.8                                       | 2.2   | 2          | 0.023                         | 0.023      | 0.023      | 0.026                            | 0.029      | 0.028      |
| Electrostatic Precipitators (ESP) | 1.5                                       | 2     | 1.75       | 0.057                         | 0.057      | 0.057      | 0.017                            | 0.034      | 0.024      |
| Reference                         | [128]                                     | [128] | Calculated | [127, 131]                    | [127, 131] | [127, 131] | [130, 131]                       | [130, 131] | [130, 131] |

Total energy and water use, as well as LCI emissions associated with metakaolin calcination are computed based on The User Input selection sheet, the LCI data collected in Table 4.8 to Table 4.11, and as described in equations (4.29) to (4.32). Firstly, total electricity use for kaolin calcination is calculated considering the electricity use of the calcination technology and the electricity use of the PM control technology, both selected by the user. Values of electricity use are then multiplied with the amount of metakaolin modeled as shown in equation (4.29):

$$\mathbf{Electricity}_{calcination} = (\mathbf{Electricity}_{calcination\ option\ i} + \mathbf{Electricity}_{PM\ control\ option\ k}) * \frac{1}{1000} * \mathbf{FU} \quad (4.29)$$

Where:

- $\mathbf{Electricity}_{calcination}$  = amount of electricity used for the calcination technology option i, including the electricity use of the PM control technology option k (kWh).
- $\mathbf{Electricity}_{calcination\ option\ i}$  = amount of electricity used for the calcination technology option i (kWh/tonne of metakaolin).
- $\mathbf{Electricity}_{PM\ control\ option\ k}$  = amount of electricity used for the PM control technology option k (kWh/tonne of metakaolin).
- $\mathbf{FU}$  = functional unit modeled (kg of metakaolin).

Secondly, electricity use for fuel preparation is computed based on the user's fuel mix input (*User-specific\_fuel\_mix* or *U.S. Average\_fuel\_mix*) and the correspondent electricity use data collected in Table 4.10. Values of electricity use for fuel preparation are then multiplied with the amount of metakaolin modeled as shown in equation (4.30):

$$\mathbf{Electricity}_{fuel\ prep} = \sum_{fuels} (\mathbf{Electricity\ use\ factor}_{fuel\ j} * \%_{fuel\ j}) * \frac{1}{1000} * \mathbf{FU} \quad (4.30)$$

Where:

- $\mathbf{Electricity}_{fuel\ prep}$  = amount of electricity used for the preparation of the fuel mix used for clay calcination (kWh).
- $\mathbf{Electricity\ use\ factor}_{fuel\ j}$  = amount of electricity used for the preparation of fuel j (kWh/tonne of metakaolin).
- $\%_{fuel\ j}$  = percentage of fuel j in the total fuel mix for clay calcination.
- $\mathbf{FU}$  = functional unit modeled (kg of metakaolin).

Subsequently, the total electricity use during calcination will include both the electricity use associated with the calcination technology and the electricity use for the fuel mix preparation as shown in equation (4.31):

$$\mathbf{Electricity}_{total, calcination} = \mathbf{Electricity}_{calcination} + \mathbf{Electricity}_{fuel prep} \quad (4.31)$$

Where:

- $\mathbf{Electricity}_{total, calcination}$  = total electricity used for the calcination technology option i, (kWh).
- $\mathbf{Electricity}_{calcination}$  = amount of electricity used for the calcination technology option i, including the electricity use of the PM control technology option k (kWh).
- $\mathbf{Electricity}_{fuel prep}$  = amount of electricity used for the preparation of the fuel mix used for clay calcination (kWh).

Finally, the total energy, water use, and emissions of a particular output (e.g., CO<sub>2</sub>, CH<sub>4</sub>, etc.) associated with the total electricity use during calcination of the raw clay are calculated using the LCI factors from electricity generation (both upstream and direct emissions) described in Section 4.1.3.3 for the electricity grid mix used at the production plant where calcination of the raw clay takes place. LCI factors from electricity generation are then multiplied by the total electricity use during calcination from equation (4.39) as shown in equation (4.32) below:

$$\mathbf{Emissions}_{output, electricity-calcination} = \mathbf{Electricity}_{total, calcination} * \mathbf{EF}_{output} \quad (4.32)$$

Where:

- $\mathbf{Emissions}_{output, electricity-calcination}$  = emissions of each output (e.g., CO<sub>2</sub>, CH<sub>4</sub>, etc.) associated with electricity consumption during calcination phase (kg).
- $\mathbf{Electricity}_{total, calcination}$  = amount of electricity used for the calcination technology option i, including the electricity use of the PM control technology option k (kWh).
- $\mathbf{EF}_{output}$  = emission factor of an output associated with electricity generation (kg output/kWh).



In order to calculate the emissions associated with fuel combustion and pre-combustion of the kiln firing system, the total thermal energy needed for clay calcination is first calculated following equation (4.33), data from Table 4.8, and *The User Input* selection on calcination technology and amount of metakaolin modeled:

$$\mathbf{Thermal\ Energy}_{total} = \mathbf{Thermal\ Energy}_{factor} * \frac{1}{1000} * \mathbf{FU} \quad (4.33)$$

Where:

- Thermal Energy<sub>total</sub> = total thermal energy needed for clay calcination (MJ).
- Thermal Energy<sub>factor</sub> = energy factor for the calcination technology option i (MJ/tonne of metakaolin).
- FU = functional unit modeled (kg of metakaolin).

Depending on the fuel mix used for kiln firing, the share of thermal energy use of each fuel from the fuel mix is calculated following equation (4.34):

$$\mathbf{Fuel\ consumption}_{fuel\ j} = (\mathbf{Thermal\ Energy}_{total} * \%_{fuel\ j}) / \mathbf{HHV}_{fuel\ j} \quad (4.34)$$

Where:

- Fuel consumption<sub>fuel j</sub> = amount of fuel j combusted (e.g., kg, liters, m<sup>3</sup>).
- Thermal Energy<sub>total</sub> = total thermal energy needed for clay calcination (MJ).
- %<sub>fuel j</sub> = percentage of fuel j in the total fuel mix for clay calcination.
- HHV<sub>fuel j</sub> = higher heating value or amount of heat released by a unit mass or volume of fuel j (MJ/kg fuel, MJ/l fuel, MJ/m<sup>3</sup> fuel).

Lastly, the total energy, water use, and emissions of a particular output (e.g., CO<sub>2</sub>, CH<sub>4</sub>, etc.) associated with the fuel mix used during calcination of the raw clay are calculated using the LCI factors from fuel pre-combustion and fuel combustion described in Section 4.1.3.1 and

Section 4.1.3.2. Fuels LCI factors are then multiplied by the total fuel consumption of each fuel during calcination from equation (4.34) as shown in equation (4.35) below:

$$Emissions_{output, fuel\ j - calcination} = Fuel\ consumption_{fuel\ j} * EF_{output} \quad (eq. 4.5) \quad (4.35)$$

Where:

|   |   |
|---|---|
| $Emissions_{output, fuel\ j - calcination}$ | = emissions of each output (e.g., CO <sub>2</sub> , CH <sub>4</sub> , etc.) associated with fuel j consumption during calcination phase (kg).   |
| $Fuel\ consumption_{fuel\ j}$               | = amount of fuel j combusted (e.g., kg, liters, m <sup>3</sup> ).   |
| $EF_{output}$                               | = emission factor of an output associated with fuel j pre-combustion and combustion (kg output/kg fuel j, kg output/l fuel j, kg output/m <sup>3</sup> fuel j) as calculated in equation (4.5). |

Additionally, particulate matter emissions as well as direct water consumption from the raw clay calcination process are calculated based on inventory data reported in Table 4.9 and Table 4.11 and following equation (4.36):

$$Emissions_{direct, calcination} = FU * EF_{output} * \frac{1}{1000} \quad (4.36)$$

Where:

|                                   |   |
|-----------------------------------|---|
| $Emissions_{direct, calcination}$ | = emissions of each output (i.e., PM, PM <sub>10</sub> , and water) associated with metakaolin calcination phase (kg).                                |
| FU                                | = functional unit modeled (kg of metakaolin).   |
| $EF_{output}$                     | = emission factor of an output (i.e., PM, PM <sub>10</sub> , and water) associated with metakaolin calcination phase (kg output/tonne of metakaolin). |

#### 4.1.4.5 Calcined Clay Cooling

Cooling of metakaolin immediately after calcination is required to avoid undesired chemical reactions that could induce the re-crystallization of calcined clays with original kaolin content as

previously demonstrated in [36]. In addition, heat recovered from the cooling of the calcined material could be used for preheating of the air used for combustion in the kiln. The cooling phase also allows the calcined clay to cool down to a temperature suitable for the subsequent production stages (e.g., storage, grinding, blending, packing). Since most of the successful industrial trials of metakaolin production have taken place in existing cement plants, the same technology for clinker cooling is considered in the metakaolin cooling phase. Because there is a lack of data on life-cycle inventory of materials, fuels, electricity, and emissions associated with metakaolin cooling after calcination, resources and emissions associated with clinker cooling were adopted in the tool and it may result in conservative estimates. The most common coolers for clinker cooling are: rotary coolers (tube coolers and planetary coolers), grate coolers (travelling grate coolers, conventional reciprocating grate coolers, modern reciprocating grate coolers), and vertical (gravity) coolers [12, 126, 128, 132-134]. Even though rotary coolers are no longer used in North America since 1990 [126] and travelling grate coolers were abandoned in 1980 due to their mechanical complexity and poor heat recovering efficiency [128], these technologies are available for the user in the MKC-Tool as other countries may still use these technologies for the industrial production of calcined clays [122]. Table 4.12 shows the inputs (i.e., electricity and water) associated with the different technology options for metakaolin cooling available in the MKC-Tool. While water consumption is not required for rotary and planetary coolers, their efficiency is enhanced by spraying water for more rapid cooling. Average values of water consumption were adapted from high and low water consumption values reported for each cooling technology in [128].

**Table 4.12** - Electricity and water use for metakaolin cooling technology options. Table ID: LCI\_Finishing\_01a

| Technology Option |                                |               |                  |                         |   |                                     |   |
|-------------------|--------------------------------|---------------|------------------|-------------------------|---|-------------------------------------|---|
| Inputs            | Unit (per tonne of metakaolin) | Rotary Cooler | Planetary Cooler | Travelling Grate Cooler | Reciprocating Grate Cooler (Conventional) | Reciprocating Grate Cooler (Modern) | Vertical Gravity Cooler with Grate Cooler |
| Electricity       | kWh                            | 4             | 1.5              | 5                       | 5   | 6                                   | 5.5                                       |
| Water             | m <sup>3</sup>                 | 0.03          | 0.02             | 0                       | 0   | 0                                   | 0   |
| Reference         | [128]                          | [128]         | [128]            | [128]                   | [128]                                     | [128]                               | [110, 128]                                |

The major process-related emission during metakaolin cooling is considered to be particulate matter (PM) from dust. Values of PM emissions could be conservatively approximated to the PM emissions from clinker cooling at industrial scale. During this process, the PM released is mostly consistent of coarser particles with only a small percentage (less than 15%) with particles smaller than 10 microns ( $\mu\text{m}$ ) [127]. To control the release of PM to the environment, two technologies commonly implemented during clinker cooling are available in the MKC-Tool (i.e., fabric filter or FF and Electrostatic Precipitators or ESP). For both technologies, The U.S. EPA Compilation of Air Pollutant Emission Factors AP-42 is used to calculate the total PM emissions

(PM<sub>Total</sub>) associated with metakaolin cooling [124]. Emissions of particulate matter with a 50% cut point size equal to or less than 2.5 µm (PM<sub>2.5</sub>) and particulate matter with a 50% cut point size equal to or less than 10 µm (PM<sub>10</sub>) are based on values published by the Portland Cement Association [127]. Table 4.13 shows the electricity use and PM emissions of these filters by tonne of calcined clay (metakaolin).

**Table 4.13** – PM emissions associated to metakaolin cooling by cooling technology option. Table ID: LCI\_Finishing\_01b

| PM Emission Control Technology Option |   |       |         |   |        |         |  |        |         |  |       |         |
|---------------------------------------|---|-------|---------|---|--------|---------|--|--------|---------|--|-------|---------|
| Technology                            | Electricity use (kWh/tonne of metakaolin) |       |         | PM <sub>10</sub> (kg/tonne of metakaolin) |        |         | PM <sub>2.5</sub> (kg/tonne of metakaolin) |        |         | PM <sub>Total</sub> (kg/tonne of metakaolin) |       |         |
|                                       | Min                                       | Max   | Average | Min                                       | Max    | Average | Min  | Max    | Average | Min  | Max   | Average |
| Fabric Filter (FF)                    | 1.8                                       | 2.2   | 2       | 0.002                                     | 0.0135 | 0.0069  | 0.0005                                     | 0.0075 | 0.00425 | 0.068  | 0.068 | 0.068   |
| Electrostatic Precipitators (ESP)     | 1   | 1.6   | 1.3     | 0.048                                     | 0.048  | 0.048   | NS   | NS     | NS      | 0.048  | 0.048 | 0.048   |
| Reference                             | [128]                                     | [128] | [128]   | [127]                                     | [127]  | [127]   | [127]                                      | [127]  | [127]   | [130]  | [130] | [130]   |

\*NS = Not specified

The total amount of metakaolin modeled by the user is then used to calculate the total electricity use during metakaolin cooling. Total electricity includes the electricity consumption of the cooling technology option selected by the user and the added electricity consumption of the PM control technology collected from *The User Input* sheet and multiplied by the electricity consumption factor from the “Cooling Inputs Inventory” section of the *Finishing* sheet (Table 4.12 and Table 4.13) as shown in equation (4.37):

$$\begin{aligned}
 & \mathbf{Electricity}_{total, cooling} \\
 & = (\mathbf{Electricity}_{cooling\ option\ i} + \mathbf{Electricity}_{PM\ control\ option\ k}) * \frac{1}{1000} * \mathbf{FU} \quad (4.37)
 \end{aligned}$$

Where:

Electricity<sub>total, cooling</sub> = amount of electricity used for the cooling technology option i, including the electricity use of the PM control technology option k (kWh).

Electricity<sub>cooling option i</sub> = amount of electricity used for the cooling technology option i (kWh/tonne of metakaolin).

Electricity<sub>PM control option k</sub> = amount of electricity used for the PM control technology option k (kWh/tonne of metakaolin).

FU = functional unit modeled (kg of metakaolin).

Subsequently, the energy use and total emissions of a particular output (e.g., CO<sub>2</sub>, CH<sub>4</sub>, etc.) associated with electricity consumption during metakaolin cooling are calculated following equation (4.38):

$$\mathbf{Emissions}_{output, cooling} = \mathbf{Electricity}_{total, cooling} * \mathbf{EF}_{output} \quad (4.38)$$

Where:

Emissions<sub>output, cooling</sub> = emissions of each output (e.g., CO<sub>2</sub>, CH<sub>4</sub>, etc.) associated with electricity consumption during cooling phase (kg).

Electricity<sub>total, cooling</sub> = amount of electricity used for the cooling technology option i, including the electricity use of the PM control technology option k (kWh).

EF<sub>output</sub> = emission factor of an output associated with electricity generation (kg output/kWh).

Additionally, particulate matter emissions as well as direct water consumption from the metakaolin cooling process are calculated based on inventory data reported in Table 4.12 and Table 4.13 and following equation (4.39):

$$\mathbf{Emissions}_{direct, cooling} = \mathbf{FU} * \mathbf{EF}_{output} * \frac{\mathbf{1}}{\mathbf{1000}} \quad (4.39)$$

Where:

|                                      |   |
|--------------------------------------|---|
| Emissions <sub>direct, cooling</sub> | = emissions of each output (i.e., PM, PM <sub>10</sub> , and water) associated with metakaolin cooling phase (kg).                                |
| FU                                   | = functional unit modeled (kg of metakaolin).   |
| EF <sub>output</sub>                 | = emission factor of an output (i.e., PM, PM <sub>10</sub> , and water) associated with metakaolin cooling phase (kg output/tonne of metakaolin). |

#### 4.1.4.6 Calcined Clay Finishing

The main consumption of electricity from metakaolin's production occurs during the finishing and grinding phases. Finishing of metakaolin includes milling, conveying, storage and/or packing.

##### i. Calcined Clay Grinding

Depending on the business model, the production of metakaolin could be performed (1) at the cement plant in parallel to the clinker production with subsequent grinding and blending with limestone and gypsum before storage and/or packing, or (2) metakaolin can be manufactured at a separate production facility and transported to either the cement plant to be blended with portland cement to produce blended cements or directly to the concrete central mix to be added to the concrete mix as a SCM before distribution. Because this production stage consists of multiple scenarios, the MKC-Tool considers two cases when metakaolin is mixed with clinker or portland cement to produce blended cements (i.e., *separate grinding - interblending with portland cement*) and one case when metakaolin is used as a SCM at the concrete plant (i.e., *not blended - mixed in at the concrete plant*). For both cases, grinding of metakaolin is considered to occur separately from clinker grinding. Even though the option of *intergrinding with clinker* is currently not included in the tool, a brief description of this technology approach for grinding of metakaolin is described below.

##### a) Intergrinding with Clinker

Production of metakaolin at industrial scale for the production of limestone calcined clays cements is in its infancy and limited to industrial trials in few countries around the world (e.g., India, Cuba, Colombia). Reported key lessons and insights on these field trials have shown that intergrinding of clinker and gypsum with metakaolin and limestone (in the case of raw limestone additions) is currently the most practical means of grinding [49]. However, for blended cements, particularly those with higher replacement ratios, especial attention should be given to avoid preferential grinding of the materials. Cements that contain partial replacements of portland cement with metakaolin and limestone could show great rate of preferential grinding which means that the softer materials (i.e., metakaolin and limestone) are overground while the harder material (i.e., clinker) is often underground. This could lead to a poorly graded cement that contains coarser clinker particles and to poor reactivity and hydration of the cement blend. On the opposite side, a cement blend that contains a great number of fines from the overly ground metakaolin and

limestone, could lead to unworkable mixes in concrete applications and a substantial increase in the overall water demand. Given the lack of control in the particle size distribution of the cement and its overall fineness when metakaolin is interground with clinker, the tool does not currently include this technology option. However, if the user would like to explore this scenario, the complete life-cycle environmental assessment could be run in the tool and the emissions from this stage can be excluded. Further impacts from intergrinding metakaolin with clinker could be included.

b) Separate Grinding and Interblending with Portland Cement

This option is available to the user when the final product is a blended cement with metakaolin and clinker (limestone and gypsum could also be added during the blending process). As mentioned before, the particle size distribution of the finished cement-based material is paramount in the potential reactivity of the cement blend and its early age hydration. A coarser material would reduce the cement’s ability to react and hydrate with other components of the mix. Contrastingly, an overly fine material would reduce workability and increase water demand which in turn could reduce the concrete’s mechanical performance. Optimal particle size distribution of these blended cements is typically achieved by separately grinding each component (i.e., clinker, metakaolin, and limestone) and then blending them together (i.e., interblending). Nonetheless, separate grinding of individual components is limited to (1) whether a spare mill or grinding system is available for metakaolin and other minerals’ individual grinding, (2) high investment costs for the adoption of secondary milling systems, (3) increased operational costs for multiple grinding systems and additional storage capacity when grinding and blending of individual materials cannot be performed at the same time [12, 132].

Grinding of metakaolin can be done by means of any of the existing grinding technologies typically used for clinker finishing and milling [135]. Grinding systems available in the MKC-Tool are: ball (tube) mill, horizontal roller mill, roller press, and vertical roller mill. Due to lack of primary data on calcined clay finishing and grinding, electricity and water inputs for clinker grinding where adapted from several published sources and data are shown in Table 4.14.

**Table 4.14** - Electricity and water use for metakaolin grinding technology options. Table ID: LCI\_Finishing\_02a

| Grinding Technology    | Electricity (kWh/tonne of cement) |            |            | Water (kg/tonne of cement)* |       |            |
|------------------------|-----------------------------------|------------|------------|-----------------------------|-------|------------|
|                        | Min                               | Max        | Average    | Min                         | Max   | Average    |
| Ball (Tube) Mill       | 30                                | 42         | 36         | 0                           | 40    | 20         |
| Horizontal Roller Mill | 21                                | 25.5       | 23.25      | 0                           | 0     | 0          |
| Roller Press           | 20                                | 24.5       | 22.25      | 0                           | 0     | 0          |
| Vertical Roller Mill   | 22                                | 28.5       | 25.25      | 0                           | 20    | 10         |
| Reference              | [126, 128]                        | [126, 128] | Calculated | [126]                       | [126] | Calculated |

\*Original water values obtained in units of liters/tonne of cement

In addition to the emissions associated with electricity generation and use during the finishing processing of metakaolin, process-based emissions from milling and grinding of metakaolin comprise mainly very fine dust particles (i.e., particulate matter or PM) whose air pollution should be adequately controlled. Due to the lack of primary data on air emissions from metakaolin grinding and handling after calcination at industrial scale, the tool has adopted particulate matter emissions associated with clinker milling and finishing. To control the release of PM to the environment, two technologies are commonly used (i.e., pulse jet bag filter or PJBF and Electrostatic Precipitators or ESP). ESPs are no longer installed in new plants but those with this control technology for PM control during grinding are still in operation. Because nowadays most cement plants use PJBF for dust control in the milling systems, this PM control technology is included in the MKC-Tool [128]. The U.S. EPA Compilation of Air Pollutant Emission Factors AP-42 is adapted to calculate the total PM emissions ( $PM_{Total}$ ) associated with metakaolin grinding [124]. Table 4.15 shows the electricity use and PM emissions of these filters by tonne of calcined clay (metakaolin).

**Table 4.15** - Electricity use and PM emissions for PM control technology during metakaolin grinding. Table ID: LCI\_Finishing\_02b

| Technology                  | Electricity use (kWh/tonne of metakaolin) |       |            | PMtotal (kg/tonne of metakaolin) |       |         |
|-----------------------------|---|-------|------------|----------------------------------|-------|---------|
|                             | Min                                       | Max   | Average    | Min                              | Max   | Average |
| Pulse Jet Bag Filter (PJBF) | 0.4                                       | 0.6   | 0.5        | 0.018                            | 0.021 | 0.020   |
| Reference                   | [128]                                     | [128] | Calculated | [130]                            | [130] | [130]   |

Calculations of total electricity includes the electricity consumption of the grinding technology option selected by the user and the added electricity consumption of the PM control technology collected from *The User Input* sheet and multiplied by the electricity consumption factor from the “Grinding Inputs Inventory” section of the *Finishing* sheet (Table 4.14 and Table 4.15) as shown in equation (4.40):

$$\begin{aligned}
 & \mathbf{Electricity}_{total, grinding} \\
 & = (\mathbf{Electricity}_{grinding\ option\ i} + \mathbf{Electricity}_{PM\ control\ option\ k}) * \frac{1}{1000} * \mathbf{FU} \quad (4.40)
 \end{aligned}$$



Where:

|  |   |
|--|---|
| Electricity <sub>total, grinding</sub>     | = amount of electricity used for the grinding technology option i, including the electricity use of the PM control technology option k (kWh). |
| Electricity <sub>grinding option i</sub>   | = amount of electricity used for the grinding technology option i (kWh/tonne of metakaolin).  |
| Electricity <sub>PM control option k</sub> | = amount of electricity used for the PM control technology option k (kWh/tonne of metakaolin).  |
| FU   | = functional unit modeled (kg of metakaolin).   |

Subsequently, the energy use and total emissions of a particular output (e.g., CO<sub>2</sub>, CH<sub>4</sub>, etc.) associated with electricity consumption during metakaolin grinding are calculated following equation (4.41):

$$\mathbf{Emissions}_{output, grinding} = \mathbf{Electricity}_{total, grinding} * \mathbf{EF}_{output} \quad (4.41)$$

Where:

|  |   |
|--|---|
| Emissions <sub>output, grinding</sub>  | = emissions of each output (e.g., CO <sub>2</sub> , CH <sub>4</sub> , etc.) associated with electricity consumption during grinding phase (kg). |
| Electricity <sub>total, grinding</sub> | = amount of electricity used for the grinding technology option i, including the electricity use of the PM control technology option k (kWh).   |
| EF <sub>output</sub>                   | = emission factor of an output associated with electricity generation (kg output/kWh).  |

Additionally, particulate matter emissions as well as direct water consumption from the metakaolin grinding process are calculated based on inventory data reported in Table 4.14 and Table 4.15 and following equation (4.42):

$$\mathbf{Emissions}_{direct, grinding} = \mathbf{FU} * \mathbf{EF}_{output} * \frac{\mathbf{1}}{\mathbf{1000}} \quad (4.42)$$

Where:

|                                       |  |
|---------------------------------------|--|
| Emissions <sub>direct, grinding</sub> | = emissions of each output (i.e., PM, PM <sub>10</sub> , and water) associated with metakaolin grinding phase (kg).                                |
| FU                                    | = functional unit modeled (kg of metakaolin).  |
| EF <sub>output</sub>                  | = emission factor of an output (i.e., PM, PM <sub>10</sub> , and water) associated with metakaolin grinding phase (kg output/tonne of metakaolin). |

c) Not blended - Mixed in at the Concrete Plant

When the location of the metakaolin production facility is separate from the cement plant, shipping of metakaolin can be done in bulk quantities or in packages of various size and shipped to the concrete plant where it is used as a supplementary cementitious material (SCM) in concrete batching and mixing. For this model of production, grinding technology options and their respective electricity use and emissions are considered to be the same as those used for the *separate grinding - interblending with portland cement* case described above in Table 4.14 and Table 4.15. Equations (4.40) - (4.42) are used to calculate the energy and water use as well as emissions associated with the grinding phase.

**ii. Conveying of Materials in the Plant**

Conveying of materials throughout each production station of metakaolin processing includes the transport of (1) raw clays from silos to the grinding station, (2) pre-milled raw clays to the kiln or flash calciner, (3) calcined clays through the cooling station, (4) cooled calcined clays to the grinding and/or blending stations, and depending on the business model, (5) finished product to silos or packaging station. At the cement plant, conveyance of raw materials, clinker, and cement within is performed using mechanical systems or pneumatic conveyance [124, 128]. Due to similarities in both the conveyance technologies used and the materials conveyed, electricity use factors for typical conveyance technologies from cement manufacturing were adopted from Gursel [110] and are available in the MKC-Tool as shown in Table 4.16.

**Table 4.16** - Electricity use for conveyance technology during material transport within the plant. Table ID: LCI\_Finishing\_04

| Conveyor Technology | Electricity (kWh/kg*m) |
|---------------------|------------------------|
| Screw pump          | 1.20E-06               |
| Airlift             | 1.10E-05               |
| Dense phase pump    | 5.90E-06               |
| Bucket elevator     | 4.10E-06               |
| Reference           | [110]                  |

For the calculation of energy and air emissions associated to conveying of materials throughout the plant, the conveyance technology and the distances traveled per each production phase are collected from *The User Input* sheet and multiplied by each electricity use factor from the *Finishing* sheet (Table 4.16) as shown in equation (4.43):

$$\begin{aligned}
 \mathbf{Electricity}_{total, conveyance\ option\ k} &= \mathbf{Mass}_{material} \\
 & * \mathbf{Distance}_{conveyance\ option\ k} \times \mathbf{EF}_{conveyance\ option\ k}
 \end{aligned}
 \tag{4.43}$$

Where:

- $\mathbf{Electricity}_{total, conveyance\ option\ k}$  = amount of electricity used for the conveyance technology option k used in each conveyance scenario (kWh).
- $\mathbf{Mass}_{material}$  = mass of material conveyed (kg).
- $\mathbf{Distance}_{conveyance\ option\ k}$  = distance traveled by conveyance technology option k (m).
- $\mathbf{EF}_{conveyance\ option\ k}$  = electricity use per unit of material and unit of distance during conveyance by option k (kWh/kg-km).

Finally, the total energy used or emissions of a particular output (e.g., CO<sub>2</sub>, CH<sub>4</sub>, etc.) is calculated following equation (4.44):

$$\mathbf{Emissions}_{output, conveyance} = \mathbf{Electricity}_{total, conveyance\ option\ k} * \mathbf{EF}_{output}
 \tag{4.44}$$

Where:

$Emissions_{output, conveyance}$  = emissions of each output (e.g., CO<sub>2</sub>, CH<sub>4</sub>, etc.) associated with electricity consumption material transport in the plant (kg).

$Electricity_{total, conveyance, option k}$  = amount of electricity used for the conveyance technology option k used in each conveyance scenario (kWh).

$EF_{output}$  = emission factor of an output associated with electricity generation (kg output/kWh).

### iii. Calcined Clay Storage

Storage of calcined clay consists of the same systems typically used to store clinker and cement [122]. The most common types of storage systems are: single cell silo with discharge hopper, single cell silo with central cone, multi-cell silo, and dome silo with central cone [128]. Because the electricity demand for each of these storage systems is very low compared to other production stages such as cooling and grinding, life-cycle inventory data is included but only considered for internal calculations in the MKC-Tool (i.e., it is not available as an option for the user in *The User Input* sheet). An average value of electricity use factor for calcined clay storage is calculated in the tool and used universally regardless of the storage system in the model. This average value has been calculated based on data reported for cement storage in [128] as shown in Table 4.17.

**Table 4.17** - Electricity use for calcined clay storage system. Table ID: LCI\_Finishing\_05

| Technology   | Electricity use (kWh/tonne of metakaolin) |       |            |
|--------------|---|-------|------------|
|              | Min                                       | Max   | Average    |
| Storage silo | 0.15                                      | 0.3   | 0.225      |
| Reference    | [128]                                     | [128] | Calculated |

The total amount of metakaolin modeled by the user is then used to calculate the total electricity for storage as shown in equation (4.45):

$$Electricity_{total, storage} = Electricity_{storage} * \frac{1}{1000} * FU \quad (4.45)$$

Where:

$Electricity_{total, storage}$  = amount of electricity used for the storage system (kWh).

Electricity<sub>storage</sub> = amount of electricity used for the storage system per tonne of metakaolin (kWh/tonne of metakaolin).

FU = functional unit modeled (kg of metakaolin).

Subsequently, the energy use and total emissions of a particular output (e.g., CO<sub>2</sub>, CH<sub>4</sub>, etc.) associated with electricity consumption during metakaolin storage are calculated following equation (4.46):

$$\mathbf{Emissions}_{output, storage} = \mathbf{Electricity}_{total, storage} * \mathbf{EF}_{output} \quad (4.46)$$

Where:

Emissions<sub>output, storage</sub> = emissions of each output (e.g., CO<sub>2</sub>, CH<sub>4</sub>, etc.) associated with electricity consumption during metakaolin storage (kg).

Electricity<sub>total, storage</sub> = amount of electricity used for the storage system (kWh).

EF<sub>output</sub> = emission factor of an output associated with electricity generation (kg output/kWh).

Similar to cement distribution, shipping of finished calcined clay can be done by bulk discharged into trucks or by packaging the material into paper bags of different sizes (e.g., 25 kg, 40 kg, and 50kg) using rotating packing machines [127]. Since bagging and pelletizing of finished calcined clay is optional and electricity use is negligible compared to other main production processes, electricity use for this phase is not included in the MKC-Tool.

#### **4.1.4.7 Non-process Related Electricity Consumption**

As described before, the most obvious areas that draw the biggest share of electricity consumption in a typical industrial production of calcined clay are the grinding of raw materials and finished metakaolin, electricity associated with plant services and office maintenance are included in the tool. Electricity consumption for non-process related use in a calcined clay facility is mainly associated with the energy use to (1) maintain the plant, (2) provide with the heating, ventilation, and air conditioning (HVAC) of different offices, (3) provide lighting in office and production stations, (4) other miscellaneous facility support. Because calcined clay production for cement manufacturing at large scale has only been recently adopted in industrial trials at several cement plants in the world, data for non-process electricity use in cement facilities is used in the tool. Values for electricity use associated with non-process power consumption were calculated based

on (1) the total cement plant power consumption in the U.S. from historical data collected from the Getting the Numbers Right (GNR) Project from the Global Cement and Concrete Association (GCCA) [16] and (2) the percentage of electricity use for HVAC systems and lighting for a typical cement plant adopted from values reported in the second edition of the Cement Plant Environmental Handbook (i.e., 7.8%) [136]. Reported values and calculations to obtain the electricity factor for non-process related electricity consumption are shown in Table 4.18 below.

**Table 4.18** – U.S. cement plant power consumption (kWh / t cement) for the years 1990, 2000, and 2005-2018. (GNR) [16]

| Year    | Total (kWh/tonne of metakaolin) |
|---------|---------------------------------|
| 1990    | 145.81                          |
| 2000    | 132.97                          |
| 2005    | 132.65                          |
| 2006    | 133.27                          |
| 2007    | 132.87                          |
| 2008    | 134.03                          |
| 2009    | 138.10                          |
| 2010    | 131.71                          |
| 2011    | 126.40                          |
| 2012    | 122.73                          |
| 2013    | 124.80                          |
| 2014    | 127.48                          |
| 2015    | 131.94                          |
| 2016    | 134.64                          |
| 2017    | 133.57                          |
| 2018    | 133.39                          |
| Average | 132.27                          |

Non-process related electricity use is calculated with the total average electricity consumption from Table 4.18 and following equation (4.47):

$$Electricity\_factor_{facility} = Electricity_{total,consumption} * \frac{1}{1000} * \%_{facility\_use} \quad (4.47)$$

Where:

- $Electricity\_factor_{facility}$  = electricity consumption associated to non-process activities in the facility (kWh/kg metakaolin).
- $Electricity_{total, consumption}$  = total electricity consumption at the metakaolin plant including electricity associated with each production phase (kWh/tonne metakaolin).
- $\%_{facility\_use}$  = percentage of electricity consumption associated to non-process related activities in the metakaolin facility. Approximately 7.8% according to [136].

Subsequently, the total amount of metakaolin modeled by the user is then used to calculate the total electricity consumption for non-process related activities as shown in equation (4.48):

$$Electricity_{total, facility} = Electricity\_factor_{facility} * FU \quad (4.48)$$

Where:

- $Electricity_{total, facility}$  = total electricity consumption associated to non-process activities in the facility (kWh).
- $Electricity\_factor_{facility}$  = electricity consumption associated to non-process activities in the facility (kWh/kg metakaolin).
- FU = functional unit modeled (kg of metakaolin).

Finally, the energy use and total emissions of a particular output (e.g., CO<sub>2</sub>, CH<sub>4</sub>, etc.) associated with electricity consumption for non-process related activities are calculated following equation (4.49):

$$Emissions_{output, facility} = Electricity_{total, facility} * EF_{output} \quad (4.49)$$

Where:

|                                 |  |
|---------------------------------|--|
| $Emissions_{output, facility}$  | = emissions of each output (e.g., CO <sub>2</sub> , CH <sub>4</sub> , etc.) associated with electricity consumption at the facility for non-process related activities (kg). |
| $Electricity_{total, facility}$ | = total electricity consumption associated to non-process activities in the facility (kWh).  |
| $EF_{output}$                   | = emission factor of an output associated with electricity generation (kg output/kWh).   |

#### 4.1.5 Total Emissions Calculations

Total air emissions as well as total energy use (electricity and fuel consumption) and water consumption are calculated for the entire life-cycle assessment within the system boundary defined in Section 4.1.1. The total emissions of a particular output (e.g., CO<sub>2</sub>, CH<sub>4</sub>, etc.) associated with the entire production of metakaolin is calculated following equation (4.50):

$$Emissions_{output, total\ life-cycle} = \sum_{production\ phases} Emissions_{output, production\ phase\ m} \quad (4.50)$$

Where:

|  |   |
|--|---|
| $Emissions_{output, total\ life-cycle}$    | = emissions of each output (e.g., CO <sub>2</sub> , CH <sub>4</sub> , etc.) throughout the entire system boundary (MJ, kg). |
| $Emissions_{output, production\ phase\ m}$ | = emissions of each output (e.g., CO <sub>2</sub> , CH <sub>4</sub> , etc.) throughout each production phase m (MJ, kg).    |

Total emissions are used to compute each of the environmental impact categories associated with metakaolin's life-cycle impact assessment following the characterization factors proposed by the Environmental Protection Agency in the Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts (TRACI) [137]. These impact categories and their potential effects in the global warming, human health, and ecosystems are described in the following section.



#### 4.1.6 Life-Cycle Impact Assessment

Life-cycle impact assessment (LCIA) is one of the final steps proposed by the International Organization for Standardization (ISO) in its 14040:2006 and 14044:2006 standards for performing life-cycle assessment [107, 108]. According to ISO 14044:2006, the impact assessment should be conducted following a methodology that best described the geographical area of the study [2]. To conduct the impact assessment the MKC-Tool follows the TRACI 2.1 methodology which stands for *Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts*. This methodology was developed by the Environmental Protection Agency in 2002 and has been updated with its latest released from 2012 [137]. TRACI 2.1 characterization factors allow to estimate the potency of the emissions on several impact categories. In order to cover a comprehensive set of environmental issues, the impact categories considered relevant to metakaolin LCIA and are included in the MKC-Tool are (1) Global Warming Potential for Air Emissions – 100 year, (2) Acidification Potentials for Air Emissions, (3) Human Health Particulate Potentials for Air Emissions, (4) Eutrophication Potentials for Air Emissions, (5) Ozone Depletion Potentials for Air Emissions, (6) Smog Formation Potentials for Air Emissions, (7) Freshwater Ecotoxicity Potentials for Urban Air Emissions, (8) Human health Cancer Potentials for Urban Air Emissions, (9) Human health Non-cancer Potentials for Urban Air Emissions, and (10) Fossil Fuel Depletion. The potential of each impact category is calculated for each production phase within the system boundary and included in the *Results* sheet of the MKC-Tool. Values are displayed in graphic and tabular format. Total energy use from electricity demand and fuel use, as well as water consumption are shown in the same sheet. Emphasis on the Global Warming Potential (GWP) is given since the emissions derived from the manufacturing of metakaolin are considered to contribute in a major capacity to the potential cause of climate change. Equation (4.51) shows how the MKC-Tool converts the inventory units of total emissions from the life-cycle system boundary to the relevant impact categories included in the model.

$$\begin{aligned} \text{Characterized unit}_{\text{impact category } n} \\ = \text{Inventory unit} * \text{Characterization factor}_{\text{impact category } n} \end{aligned} \quad (4.51)$$

Where:

|  |  |
|--|--|
| Characterized unit <sub>impact category n</sub>      | = characterized unit from an impact category n (kg CO <sub>2</sub> -eq, kg SO <sub>2</sub> -eq, kg O <sub>3</sub> -eq, etc).   |
| Inventory unit                                       | = equivalent to the variable <i>Emissions</i> output, production phase m. emissions of each output (e.g., CO <sub>2</sub> , CH <sub>4</sub> , etc.) throughout each production phase m (MJ, kg). |
| Characterization factor <sub>impact category n</sub> | = equivalent factor corresponding to an impact category n (kg CO <sub>2</sub> -eq/kg, kg SO <sub>2</sub> -eq/kg, kg O <sub>3</sub> -eq/kg, etc).   |

## **Chapter 5 – MKC-LCA Tool Application and Results Comparison**

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This chapter describes how the MKC-LCA Tool can be used to model the global warming potential (GWP) and energy demand of metakaolin for different scenarios of calcination technology and fuel mix input. Emphasis on GWP and energy demand is given since the emissions derived from the manufacturing of metakaolin are considered to contribute in a major capacity to the potential cause of climate change. In addition, cement blends with a fixed ratio of replacement with metakaolin and limestone are also presented and evaluated against portland cement and commercially available blended cements in California. With eight cement plants distributed along the state and an annual production of 9.4 million tons of clinker in 2017 [3], California is the second largest cement producing state in the United States after Texas. The consequential life-cycle assessment described in this chapter answers the question of how likely it is that cement-based materials comprising metakaolin, limestone, and portland cement have lower environmental impact than conventional blended cements and/or portland cement. A consequential life-cycle assessment differs from a traditionally attributional LCA in that the former's goal is to describe how relevant flows within the system boundary of an LCA will change in response to alternative scenarios or decisions [138].

### **5.1 Case Study 1: GWP and Energy Demand of Metakaolin Production in California**

With the aim to investigate the environmental impacts of metakaolin production, the MKC-LCA Tool was used to model the GWP and the energy demand of metakaolin for different scenarios of calcination technology and fuel mix input. Extraction and production of metakaolin was assumed to be done in California. Modeling parameters were assigned following the assumptions detailed in Table 5.1. Transportation of the raw materials (i.e., raw kaolinite clay) from the mining site to the processing plant was modeled by means of truck class 8b (model 2005) [115] for a distance of 20 km. In addition, conveyance technology option for transportation of materials throughout every production station was assumed to be done by screw pumps with a standard distance of 20 meters.

**Table 5.1** - Assumptions for MKC-LCA Tool and LCA calculations.

| <b>Technology options for:</b>                     | <b>Type of technology selected:</b>  | <b>Electricity grid mix from:</b> | <b>Process-related PM control: (when applicable)</b> |
|--|--|-----------------------------------|--|
| Extraction process for kaolin clay                 | Open pit extraction  | California, U.S.                  |  |
| Raw material drying and pre-milling                | Ball mill dry grinding   | California, U.S.                  | Fabric filter (FF)                                   |
| Raw material calcination                           | (1) Dry rotary kiln  | California, U.S.                  | Fabric filter (FF)                                   |
|  | (2) Flash calciner   | California, U.S.                  |  |
| Fuel types for dry rotary kiln                     | (1) CA average fuel mix<br>(2) Coal<br>(3) Petcoke<br>(4) Waste tires                                      | N.A.                              |  |
| Fuel types for flash calciner                      | (1) CA average fuel mix<br>(2) Coal<br>(3) Petcoke<br>(4) Natural gas<br>(5) Waste tires<br>(6) Waste wood | N.A.                              |  |
| Calcined clay cooling technology                   | Rotary cooler  | California, U.S.                  | Electrostatic precipitators (ESP)                    |
| Grinding and blending with portland cement clinker | Not blended - mixed in at the concrete plant   | California, U.S.                  |  |
| Calcined clay grinding technology                  | Ball (tube) mill   | California, U.S.                  | Pulse Jet Bag Filter (PJBF)                          |

Portland cement was modeled as ASTM Type II as this is the most common type of cement commercially available in California. Life-cycle inventory data were used from the Green Concrete LCA Web Tool developed by Gursel and Horvath [139] to model the GWP and energy demand of portland cement on mass basis (i.e., kg CO<sub>2</sub> eq/tonne and MJ/tonne respectively). Assumptions and modeling parameters to calculate the GWP and energy demand of portland cement are summarized in Table 5.2.

**Table 5.2** – Modeling parameters for portland cement’s life-cycle assessment.

| <b>Technology options for:</b>                 | <b>Type of technology selected:</b>  | <b>Electricity grid mix from:</b> |
|--|--|-----------------------------------|
| Cement raw materials mining                    | N.A.   | California                        |
| Gypsum quarry and processing plant             | N.A.   |                                   |
| Cement raw materials prehomogenization         | Dry, raw storing, preblending  |                                   |
| Cement raw materials grinding                  | Dry, raw grinding, ball mill   |                                   |
| Cement raw materials blending / homogenization | Dry, raw meal blending, and storage  |                                   |
| Clinker pyroprocessing                         | Preheater/Precalciner kiln with (1) CA average kiln fuel mix and (2) Petcoke |                                   |
| Clinker cooling                                | Reciprocating Grate Cooler (Modern)  |                                   |
| Cement finish milling / grinding / blending    | Ball Mill  |                                   |
| Conveying within the cement plant              | Screw pump, 20 m   |                                   |
| Cement PM control technology                   | Electrostatic precipitators (ESP)  |                                   |

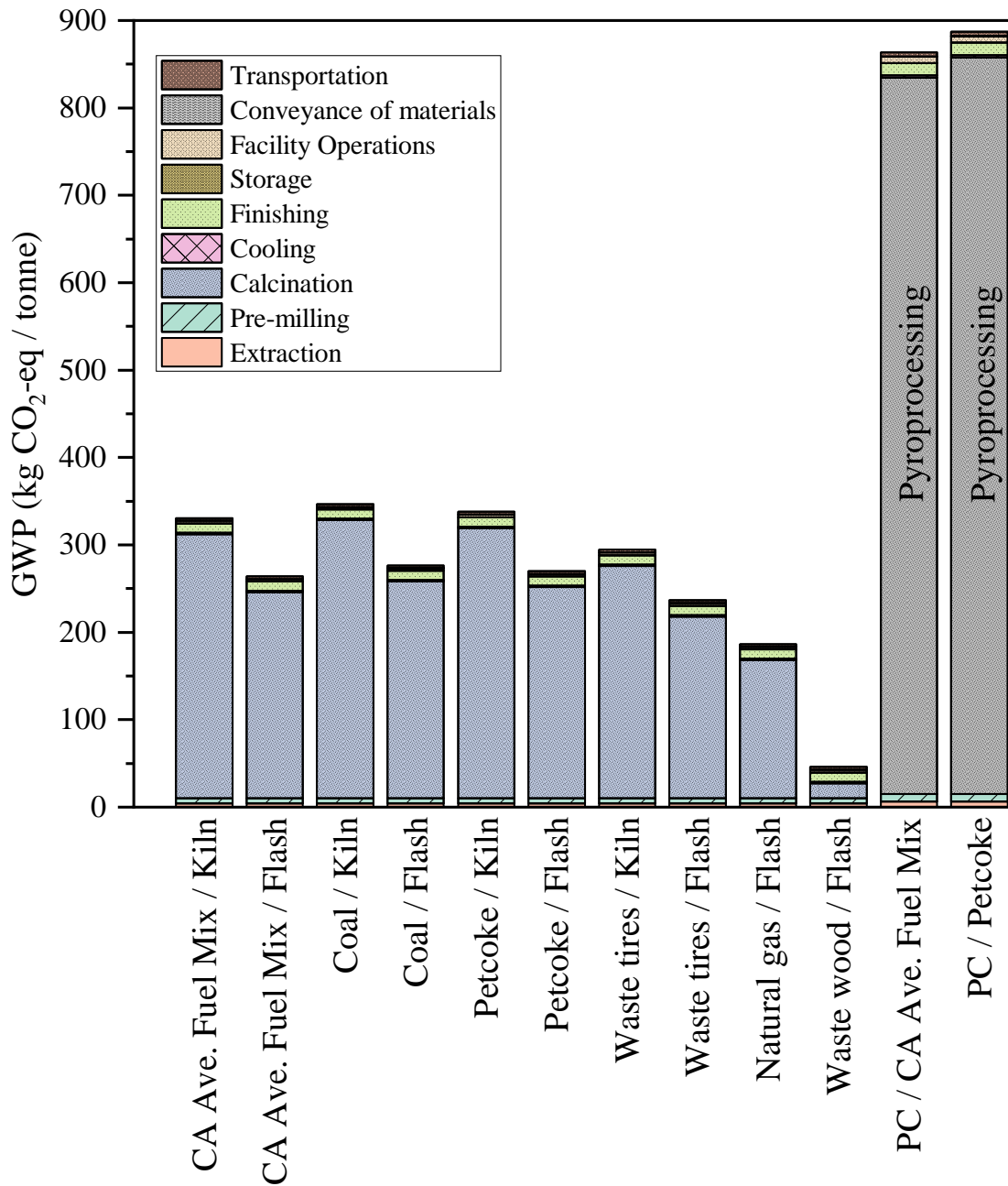
The average kiln fuel mix used in the model corresponds to the average fuel mix used in cement kilns in California. California’s cement plants and their location are detailed in Table A. 7 in the Appendix section and the average fuel mix used in the model for Case Study 1 and Case Study 2 is shown in Table A. 8 of the same section. Table 5.3 shows the transportation modes and distances traveled for metakaolin and cement production. Note that for this case study, the metakaolin production occurs at an independent facility different from the cement plant. At industrial scale, metakaolin can either be processed at a different processing plant or at the cement plant as an independent line running in parallel with clinker production.

**Table 5.3** – Transportation modes and traveled distances for metakaolin and cement production.

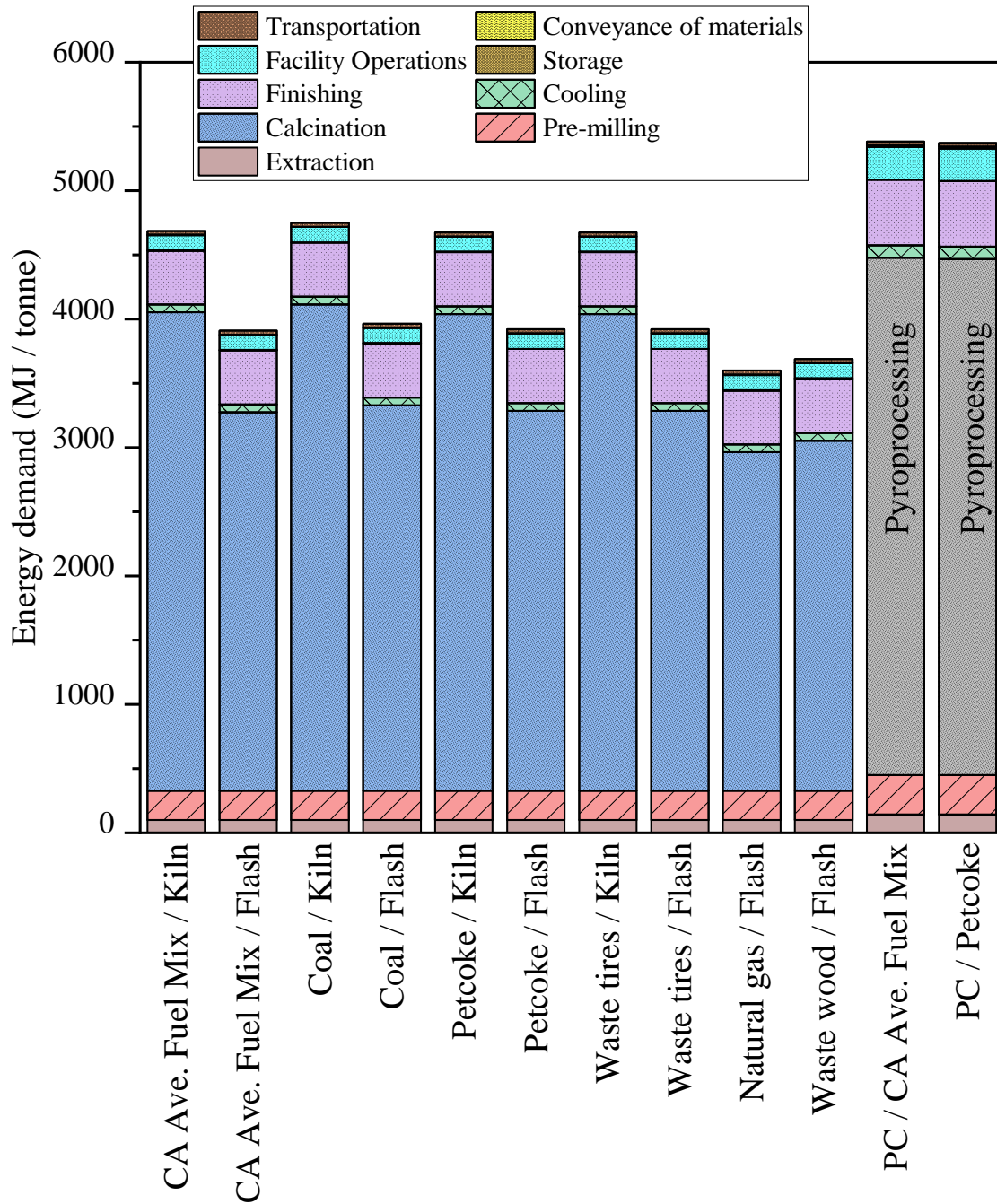
| <b>Transportation input:</b>                           | <b>Transportation mode:</b> | <b>Distance traveled (km):</b> |
|--|-----------------------------|--------------------------------|
| Kaolin (raw clay) from mining site to processing plant | Truck class 8b (Model 2005) | 20                             |
| Cement raw materials from quarry to cement plant       | Truck class 8b (Model 2005) | 20                             |
| Gypsum from processing plant to cement plant           | Truck class 8b (Model 2005) | 100                            |

Total GWP (kg CO<sub>2</sub>-eq/tonne of metakaolin) for six types of fuel used during calcination is shown in Figure 5.1. The GHG emissions from metakaolin production are directly related to the type of fuel used during calcination and the calcination technology as stated by Habert et al. [23]. For comparison, GHG emissions associated with the production of ASTM portland cement Type II in California using both the CA average kiln fuel mix and 100% petcoke are included in Figure 5.1. It is worth noting that no matter the fuel input used during calcination, metakaolin processing results in less than half of the emissions produced by traditional portland cement. The reduction in emissions comes mainly from the reduced energy needed to fire the raw materials (e.g., raw kaolinitic clay is calcined at a temperature range of 750-800°C compared to 1450°C for clinker formation). By unit mass of metakaolin, calcination with coal as an energy source in conventional cement rotary kilns shows the largest GWP with 347 kg CO<sub>2</sub>-eq/tonne of metakaolin, whereas the lowest value of GWP corresponds to waste wood with 46 kg CO<sub>2</sub>-eq/tonne of metakaolin. The results are comparable to those reported in literature. For instance, Heath et al. [70] mentioned the use of natural gas for calcination and NLK [71] used waste bitumen as a secondary fuel input. Habert et al. [23] stated the use of biogas to calcine the clay, as done at a plant in France. However, the methodology used by each author is not fully detailed. Nevertheless, investing in the best available technology for clay calcination (i.e., flash calciner) could reduce the GHG intensity of metakaolin's life-cycle by 20% when compared to the emissions produced with dry kilns using the same average fuel mix. Furthermore, a reduction of 16% is observed even when the fuel mix in the flash calciner comprises 100% coal and 18% reduction when the fuel mix comprises 100% petcoke which is the most common fuel used currently in CA. Significant reductions could be achieved when the production of metakaolin is done by means of flash calciner and biomass (e.g., waste wood), in which case the life cycle emissions are 86% lower than those from the baseline performance (i.e., dry rotary kiln with the CA average kiln fuel mix).

The importance of the calcination stage in metakaolin's life-cycle energy demand (MJ/tonne) is also evident, as shown in Figure 5.2. Lower values of energy demand than for portland cement are observed for all scenarios modeling metakaolin's production. This is expected since the lower temperatures of calcination require less fuel-derived energy, hence producing lower energy values throughout the life cycle of metakaolin. Because the energy demand of metakaolin's life cycle depends greatly on the calcination stage, there is significant potential for energy reduction when comparing the use of flash calciners and waste wood with the baseline scenario of rotary kilns and CA average fuel mix (i.e., 22% reduction in energy demand). A reduction in energy demand is directly related to a reduction in costs from fuel purchase. Hence there is economic incentive to increase the rate of adoption of this SCM in the production of blended cements.



**Figure 5.1** – GHG emissions in kg CO<sub>2</sub>-eq/tonne of metakaolin’s life-cycle assessed for varying types of fuel used during calcination and two calcination technologies (i.e., dry rotary kiln and flash calciner). Values are compared with the GHG emissions from portland cement production. All the scenarios are modeled in California. CA Ave. Fuel Mix = average fuel mix used in rotary kilns in California; Kiln = dry rotary kiln; Flash = flash calciner.



**Figure 5.2** – Energy demand in MJ/tonne of metakaolin’s life-cycle assessed for varying types of fuel used during calcination and two calcination technologies (i.e., dry rotary kiln and flash calciner). Values are compared with the energy demand from portland cement production. All the scenarios are modeled in California. CA Ave. Fuel Mix = average fuel mix used in rotary kilns in California; Kiln = dry rotary kiln; Flash = flash calciner.

## 5.2 Case Study 2: GWP and Energy Demand of Typical Blended Cements in California

The substitution of clinker with mineral additions that are either cementitious or pozzolanic is a common practice in Europe and to a lesser extent in North America. Blended cements in the United States are specified according to the standards ASTM C150 and ASTM C595. However, the most common mineral materials specified in those standards correspond to ground granulated blast furnace slag (GGBFS) and fly ash (e.g., slag modified portland cement I (SM), portland pozzolan cement IP/P, etc.). As explained in Chapter 2, the availability of these materials is limited, thus they alone do not contribute to a long-term solution in reducing clinker content in cement-based materials to improve cement's environmental impact and to meet carbon reduction targets. Table 5.4 shows the most recent data on the market share of different types of cement sold in the United States in 2017 [3]. Blended cements constituted only 2.1% of the total 2017 sales of cement in the country, whereas portland cement (Types I to V) dominates the market with more than 90% of the total sales during the same year. Because the reduction of the clinker-to-cement ratio is one of the most significant strategies to mitigate cement's environmental burden worldwide [25], this case study aims to compare the GHG emissions and energy demand of the most common blended cements in the United States (i.e., slag-modified portland cement I (SM), portland blast furnace slag cement IS, slag cement S, pozzolan modified portland cement I (PM), and portland pozzolan cement IP/P) with those from ternary blends of cement made with clinker, metakaolin, and limestone. For completion, the environmental impact of portland cement is also included in the model. A breakdown of each cement's components by mass per unit weight of cement is shown in Table 5.5 based on average values specified in ASTM C150 and ASTM C595 [140, 141]. To understand the differences in each cement's environmental impact, the modeling parameters corresponding to the technology used for clinker production, calcination of SCMs—when applicable—and fuel mix used during those processes is kept constant in all the modeled scenarios as shown in Table 5.6. In view of this, extraction of raw materials and production of all the cements were modeled in California. For cements containing metakaolin and limestone, two calcination scenarios are modeled with the CA average fuel mix (i.e., dry rotary kiln and flash calciner). Technology inputs for clinker production are the same as those from the case study 1 for all blended cements and detailed in Table 5.2. In addition, metakaolin and limestone are modeled to be processed at the cement plant and blended with cement at the last stage of production (i.e., separate grinding - interblending with portland cement). Table 5.7 shows the transportation modes and travel distances for all cement-based materials' production.



**Table 5.4** – 2017 portland cement sales in the United States by type of cement. Source: USGS, Minerals Yearbook: Cement 2017 [3].

| Type of Cement                                 | Thousand Metric Tons | Market Share |
|--|----------------------|--------------|
| Portland cement Type I and II                  | 71,700               | 75.9%        |
| High early strength (Type III)                 | 2,980                | 3.2%         |
| Sulfate resisting (Type V)                     | 15,000               | 15.9%        |
| Block  | 106                  | 0.1%         |
| Oil well                                       | 1,690                | 1.8%         |
| White  | 880                  | 0.9%         |
| Blended: <sup>a</sup>                          |                      |              |
| Portland, natural pozzolans                    | 44                   | 0.0%         |
| Portland, ground granulated blast furnace slag | 662                  | 0.7%         |
| Portland, fly ash                              | 661                  | 0.7%         |
| Portland, other pozzolans <sup>b</sup>         | 672                  | 0.7%         |
| Total blended                                  | 2,040                |              |
| Miscellaneous                                  | 24                   | 0.0%         |
| Grand total <sup>c</sup>                       | 94,500               | 100%         |

<sup>a</sup> Cements sold under ASTM C595 and those under ASTM C1157 that contain pozzolans.

<sup>b</sup> Includes blends with cement kiln dust, silica fume, other pozzolans, limestone and blends containing multiple pozzolans.

<sup>c</sup> May not add to totals shown because of independent rounding.

**Table 5.5** – Cement types under study and their constituents by mass per unit weight of cement. Average values are adopted from U.S. Standards ASTM C150, C595 as detailed by Boesch and Hellweg, 2010 [13].

| Cement Types                          | Clinker (kg) | Gypsum (kg) | GGBFS (kg) | Fly Ash (kg) | MK (kg) | Limestone (kg) |
|---------------------------------------|--------------|-------------|------------|--------------|---------|----------------|
| Portland cement Type II               | 0.950        | 0.050       | 0.000      | 0.000        | 0.000   | 0.000          |
| Slag modified portland cement I (SM)  | 0.808        | 0.043       | 0.150      | 0.000        | 0.000   | 0.000          |
| Portland blast furnace slag cement IS | 0.499        | 0.026       | 0.475      | 0.000        | 0.000   | 0.000          |
| Slag cement S                         | 0.143        | 0.008       | 0.850      | 0.000        | 0.000   | 0.000          |

|   |       |       |       |       |       |       |
|---|-------|-------|-------|-------|-------|-------|
| Pozzolan modified portland cement I (PM)    | 0.855 | 0.045 | 0.000 | 0.100 | 0.000 | 0.000 |
| Portland pozzolan cement IP/P               | 0.689 | 0.036 | 0.000 | 0.275 | 0.000 | 0.000 |
| Metakaolin and limestone cement (35MK:15LS) | 0.475 | 0.025 | 0.000 | 0.000 | 0.350 | 0.150 |

**Table 5.6** – Fuel mix input and pyroprocessing technology for cements’ life-cycle assessment in case study 2.

| <b>Scenario No.</b> | <b>Cement Type</b>                       | <b>Fuel Mix / Technology Type</b>            |
|---------------------|--|--|
| 1                   | Portland cement Type II                  | CA Ave fuel mix / Preheater/Precalciner kiln |
| 2                   | Slag modified portland cement I (SM)     | CA Ave fuel mix / Preheater/Precalciner kiln |
| 3                   | Portland blast furnace slag cement IS    | CA Ave fuel mix / Preheater/Precalciner kiln |
| 4                   | Slag cement S                            | CA Ave fuel mix / Preheater/Precalciner kiln |
| 5                   | Pozzolan modified portland cement I (PM) | CA Ave fuel mix / Preheater/Precalciner kiln |
| 6                   | Portland pozzolan cement IP/P            | CA Ave fuel mix / Preheater/Precalciner kiln |
| 7                   | 35MK15LS                                 | CA Ave fuel mix / Dry rotary kiln            |
| 8                   | 35MK15LS                                 | CA Ave fuel mix / Flash calciner             |

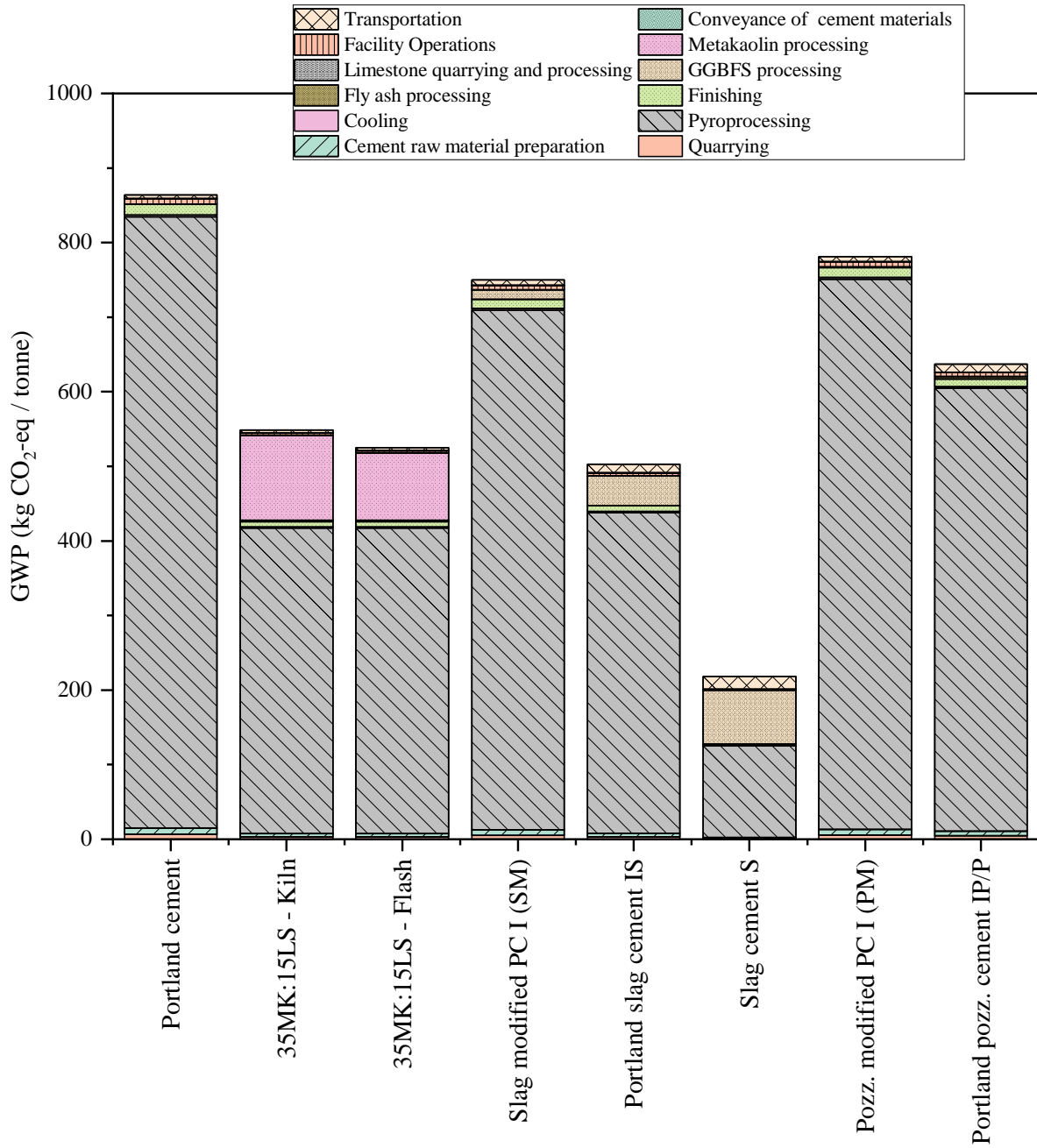
**Table 5.7** - Transportation modes and traveled distances for cement-based materials' production.

| <b>Transportation input:</b>                                      | <b>Transportation mode:</b> | <b>Distance traveled (km):</b> |
|---|-----------------------------|--------------------------------|
| Portland cement raw materials from quarry to cement plant         | Truck class 8b (Model 2005) | 20                             |
| Gypsum from processing plant to cement plant                      | Truck class 8b (Model 2005) | 100                            |
| Fly Ash to cement plant (if blended cement)                       | Rail                        | 1000                           |
| Granulated blast furnace slag to cement plant (if blended cement) | Truck class 8b (Model 2005) | 150                            |
| Kaolin (raw clay) from mining site to cement plant                | Truck class 8b (Model 2005) | 20                             |
| Kaolin (raw clay) from mining site to cement plant                | Truck class 8b (Model 2005) | 20                             |
| Limestone from quarry to cement plant                             | Truck class 8b (Model 2005) | 20                             |

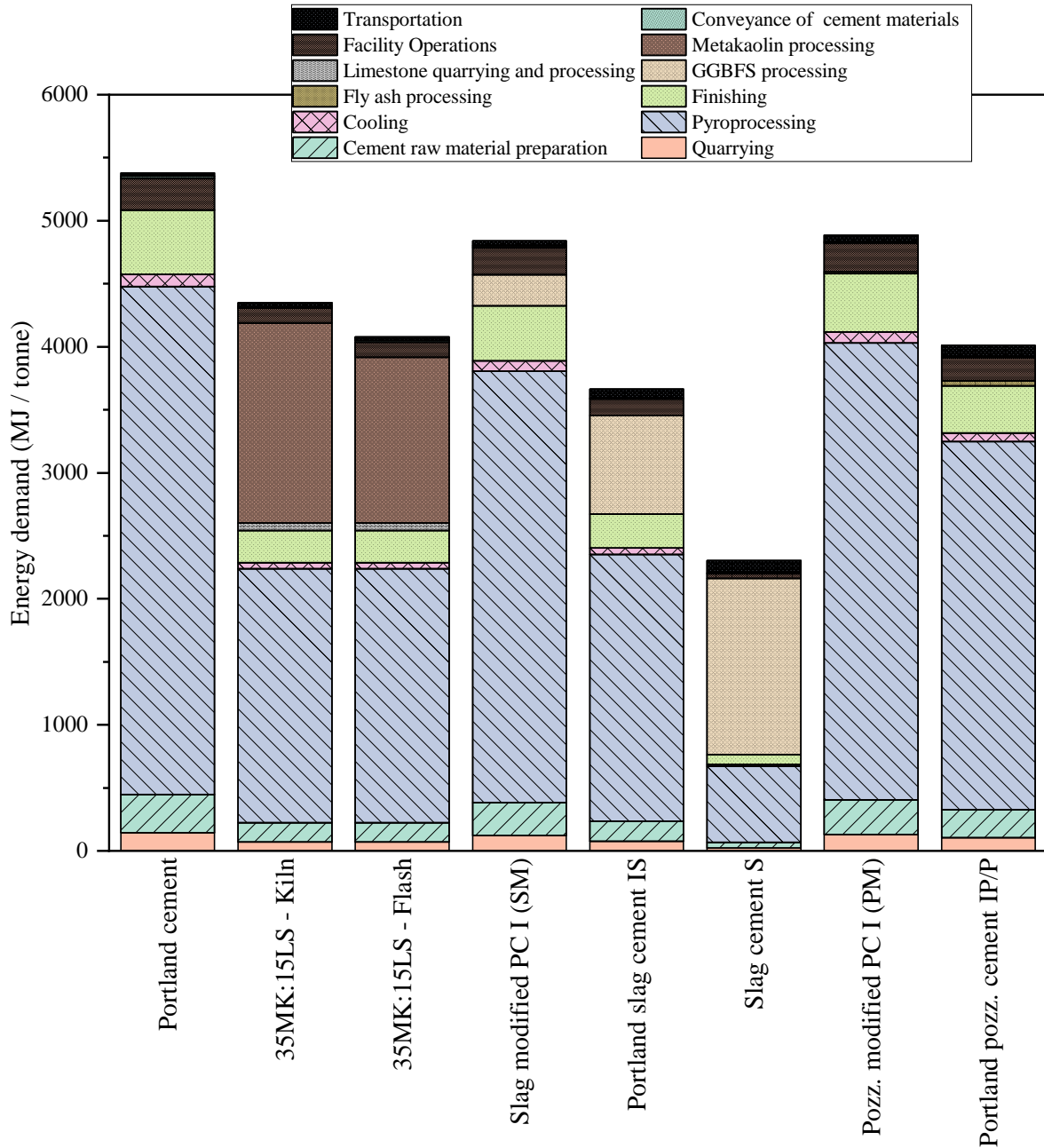
Figure 5.3 and Figure 5.4 show the total GWP and energy demand per tonne of each blended cement modeled. Compared to portland cement, ternary cements made with metakaolin and limestone in a 35:15 replacement ratio showed a significant reduction of GHG emissions and life-cycle energy demand (i.e., 36% lower emissions and 19% lower energy demand when metakaolin was calcined using a dry rotary kiln and 39% lower GHG emissions and 24% lower energy demand when using a flash calciner). This is particularly interesting given that significant reduction in GHG emissions and energy demand could still be achieved by repurposing decommissioned rotary kilns without investing in the best available technology (i.e., flash calciners). Further reductions in GHG emissions and energy demand when using a flash calciner for clay calcination would be approximately 3% and 5% (i.e., 39% GWP reduction and 24% energy reduction), respectively. When compared to commercially available blended cements, these ternary blends of cement with metakaolin and limestone showed the lowest GWP, and energy demand was only surpassed by slag cement (S) since the latter comprises an average replacement ratio of 85% of clinker by slag which results in cement with the lowest GWP and energy demand. The global warming potential of portland slag cement IS with 47.5% slag and 52.5% PC was only 9% lower than that of 35MK:15LS (i.e., 503 kg CO<sub>2-eq</sub>/tonne vs 549 kg CO<sub>2-eq</sub>/tonne). These two cement blends consisted of a similar amount of total replacement of portland cement with a supplementary cementitious material. However, at industrial scale, the lack of readily available slag worldwide renders this SCM incapable of meeting the high demand of cement. Furthermore, the GHG intensity of both cements become even more similar when the metakaolin in 35MK:15LS cement is calcined by means of flash calciner (i.e., only 4% higher GWP). Finally, all of the blended cements containing fly ash (i.e., PC I (PM) and IP/P) showed higher GHG intensities compared to 35MK:15LS cement due to their higher cement content and lower replacement ratios with SCMs (i.e., 27.5% and 72.5%). Similar energy demands are obtained when comparing 35MK:15LS with portland pozzolan cement IP/P (only 8% difference). However, the total replacement of clinker by SCMs is almost twice the amount by weight of binder for the 35MK:15LS than for the IP/P cement, which indicates a better use of raw materials and lower GHG emissions. Ultimately, the use of commercially available blended cements faces a hindrance

in availability of the SCMs commonly used in their formulations (i.e., slag, fly ash), and those alone may not meet the reduction targets set forth in the IPCC and UNEP reports for the cement industry by 2050.

In general, cement blends that contain metakaolin and limestone as partial replacement of cement could potentially reduce the GHG emissions from cement manufacturing by 5% to 40% depending on the overall replacement ratio and the availability of other SCMs that do not need to be processed (i.e., calcined at high temperatures) to exploit their pozzolanicity and react with clinker during hydration of cement. However, SCMs such as fly ash and slag are limited to the production of coal-fired energy and steel by means of arc furnace, both methods which are in decline worldwide, especially in California. Note that the conclusions made in this chapter could not be drawn when considering these cements in concrete applications since other parameters should be taken into consideration such as mix designs, strength targets, curing time, unreinforced or reinforced applications, environmental exposure and durability of the concrete members, which are not included in the previous assessment. Worldwide analysis could be done in the future, but it has been excluded from this chapter due to the ample variability in the data and the uncertainty that exists during each production process at industrial scale.



**Figure 5.3** – GHG emissions in kg CO<sub>2</sub>-eq/tonne of commercial blended cements and cement with metakaolin and limestone. Cements containing metakaolin considered two calcination technologies (i.e., dry rotary kiln and flash calciner). Values are compared with the GHG emissions from portland cement production. All the scenarios are modeled in California with the average fuel mix used in rotary kilns in California; Kiln = dry rotary kiln; Flash = flash calciner.



**Figure 5.4** – Energy demand in MJ/tonne of commercial blended cements and cement with metakaolin and limestone. Cements containing metakaolin considered two calcination technologies (i.e., dry rotary kiln and flash calciner). Values are compared with the energy demand from portland cement production. All the scenarios are modeled in California with the average fuel mix used in rotary kilns in California; Kiln = dry rotary kiln; Flash = flash calciner.

# Chapter 6 – Uncertainty Assessment

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## 6.1 Sensitivity analysis

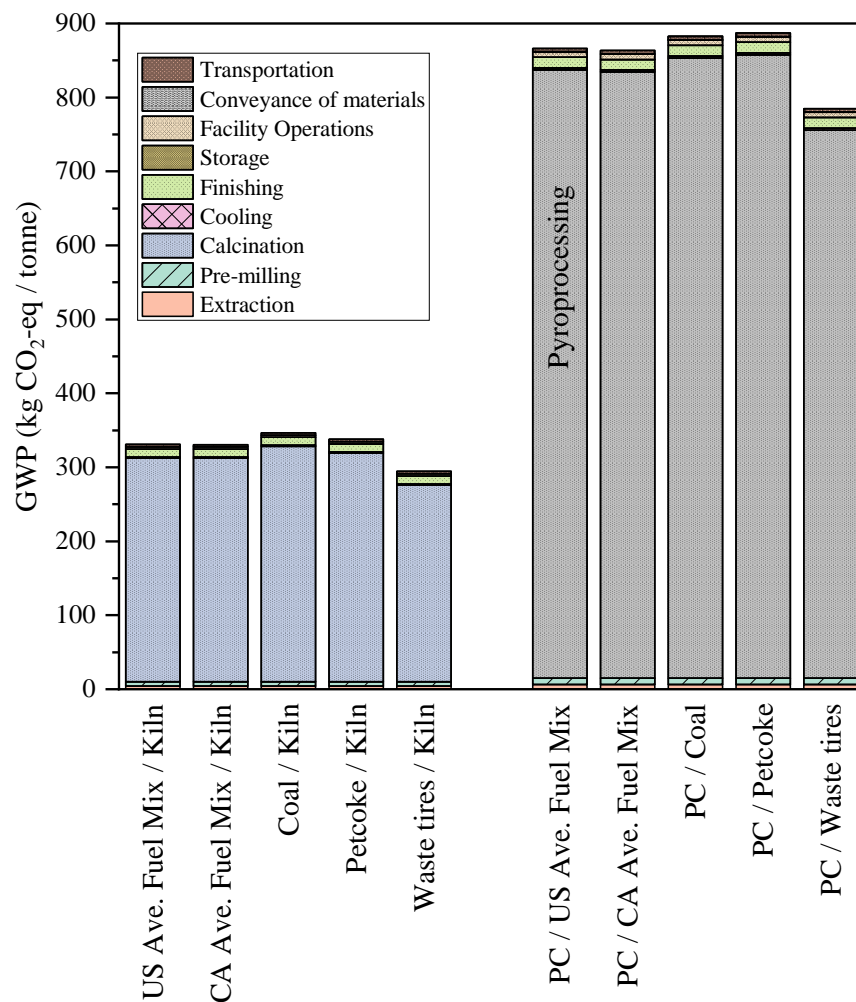
Sensitivity analysis is often done in life-cycle assessments to evaluate the robustness of a model, its life-cycle inventory, and methods by changing the input data to assess how a particular product or production process stacks up against a selected reference point (e.g., portland cement), or against the rest of potential options (e.g., blended cements containing other commercially available SCMs such as slag or fly ash), especially when using LCA as a tool for decision making [2]. The following sections contain three different cases in which a sensitivity analysis has been performed to determine whether the GHG emissions and the energy demand are susceptible to changes in model parameters and to assess whether the conclusions drawn in the case studies developed in Chapter 5 are still relevant for the feasibility for industrial application of cement blends made with metakaolin and limestone.

### 6.1.1 Influence of Fuel Mix Input on the GWP and Energy Demand of Metakaolin Production

In order to determine the potential effects on the results obtained in the MKC-Tool when modeling metakaolin production, a sensitivity analysis is performed where changes in a single input variable (fuel mix) are performed and the results are evaluated against the conclusions drawn in Chapter 5. The variability in the inputs available to the user could influence the total GHG emissions and energy demand of the model. However, as shown in Chapter 5, the GWP and energy demand are mostly influenced by the fuel mix input used for calcination of the raw clay and in the pyroprocessing of clinker during cement manufacturing. Figure 6.1 shows the life-cycle GHG emissions of metakaolin's production in California while varying the type of fuel used for calcination. Even though the calcination process is the most relevant and energy intensive in the metakaolin's production chain, the results compared to portland cement do not vary greatly and the overall trend is unchanged. Total GWP of metakaolin production in California ranges from 295 kg CO<sub>2-eq</sub>/tonne to 350 kg CO<sub>2-eq</sub> /tonne. Significant reductions are observed when the calcination process is performed by means of the best available technology (i.e., flash calciner) and the use of waste biomass for calcination (46 kg CO<sub>2-eq</sub> /tonne). For completeness, the average fuel mix used in the United States is also modeled and included in the results in Figure 6.1 and Figure 6.2. California's average fuel mix for kiln firing comprises mostly coal (58%), petroleum coke (i.e., petcoke – 24%), and waste tires (6%) that could be acquired whole or shredded. Additional energy should be considered for processing whole waste tires if they arrived at the manufacturing plant in such condition. However, for simplicity, all case studies modeled herein assumed the tires are shredded. On the other hand, the United States average fuel mix (Table 4.10) is composed mainly of bituminous coal (64%) and petcoke (21%) which explains the slight difference in the GHG emissions produced during metakaolin calcination when comparing both fuel mix inputs. Even though a transition to increased use of waste tires for fuel during calcination could lead to small savings in energy (i.e., 0.3%), the reduction in GHG emissions is still significant (i.e., 11%) from this production stage as shown in both figures. Furthermore, the use of conventional fossil fuels for kiln firing represents 25-30% of the cement production costs [15, 142-144]. The potential replacement of conventional fossil fuels with alternative waste fuels (e.g., waste tires) for kiln

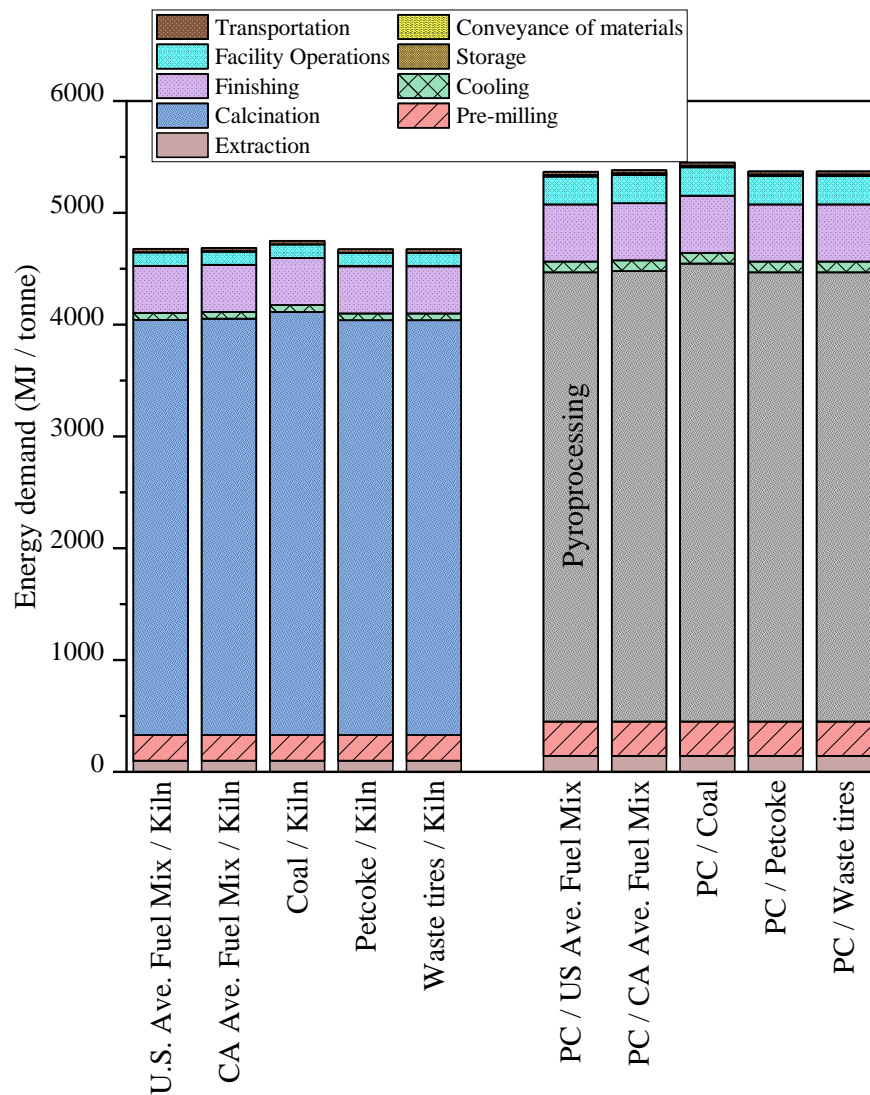
firing has been estimated to reach an average of 12% worldwide, with potentially higher replacement ratios in developing countries, therefore, adding an economic incentive due to the reduction in fuel purchase cost [142]. More energy savings are expected when using waste biomass, such as waste wood for fuel calcination, as it was shown in Figure 5.1 in Chapter 5.

Energy demand and GHG emissions from transportation are the same for metakaolin manufacturing since the variations that occur in the production technology and transportation distances of raw materials for portland cement production within the system boundary are considered similar to those for MK production. Thus, the sensitivity analysis did not consider variation in transportation distances as those do not show a significant influence in the overall results. However, when biomass is used in great quantities as the principal fuel for calcination, impacts from transportation could start playing a more significant role in the overall energy demand and climate change impacts.



**Figure 6.1** – Influence of fuel mix input on the GWP of metakaolin production. Values are compared with the GWP of portland cement production. US Ave. Fuel Mix = average fuel mix used in rotary kilns in the United States; CA Ave. Fuel Mix = average fuel mix used in rotary kilns in California; Kiln = dry rotary kiln.





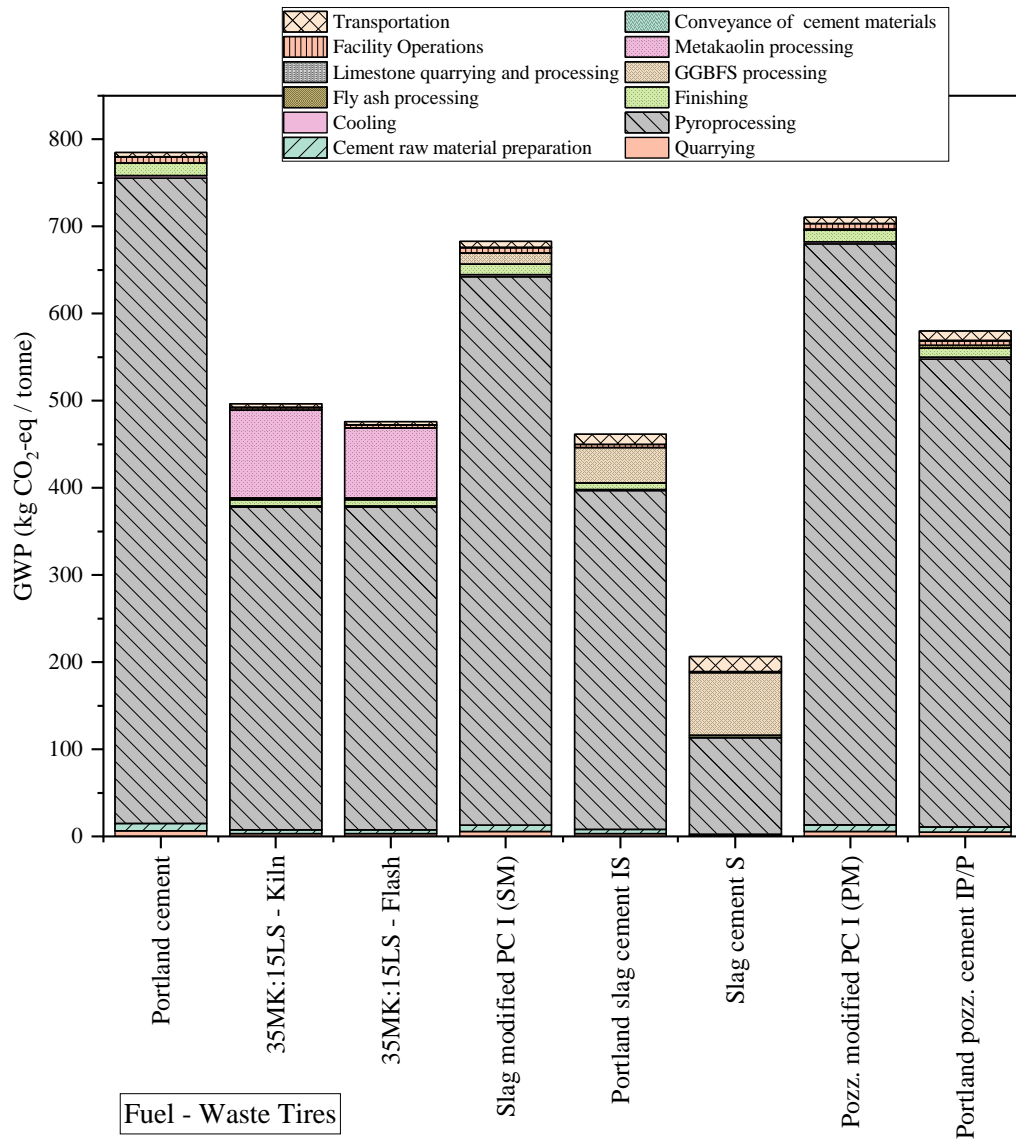
**Figure 6.2**– Influence of fuel mix input on the energy demand of metakaolin production. Values are compared with the energy demand of portland cement production. US Ave. Fuel Mix = average fuel mix used in rotary kilns in the United States; CA Ave. Fuel Mix = average fuel mix used in rotary kilns in California; Kiln = dry rotary kiln.

### 6.1.2 Influence of Fuel Mix Input on the GWP and Energy Demand of Blended Cements

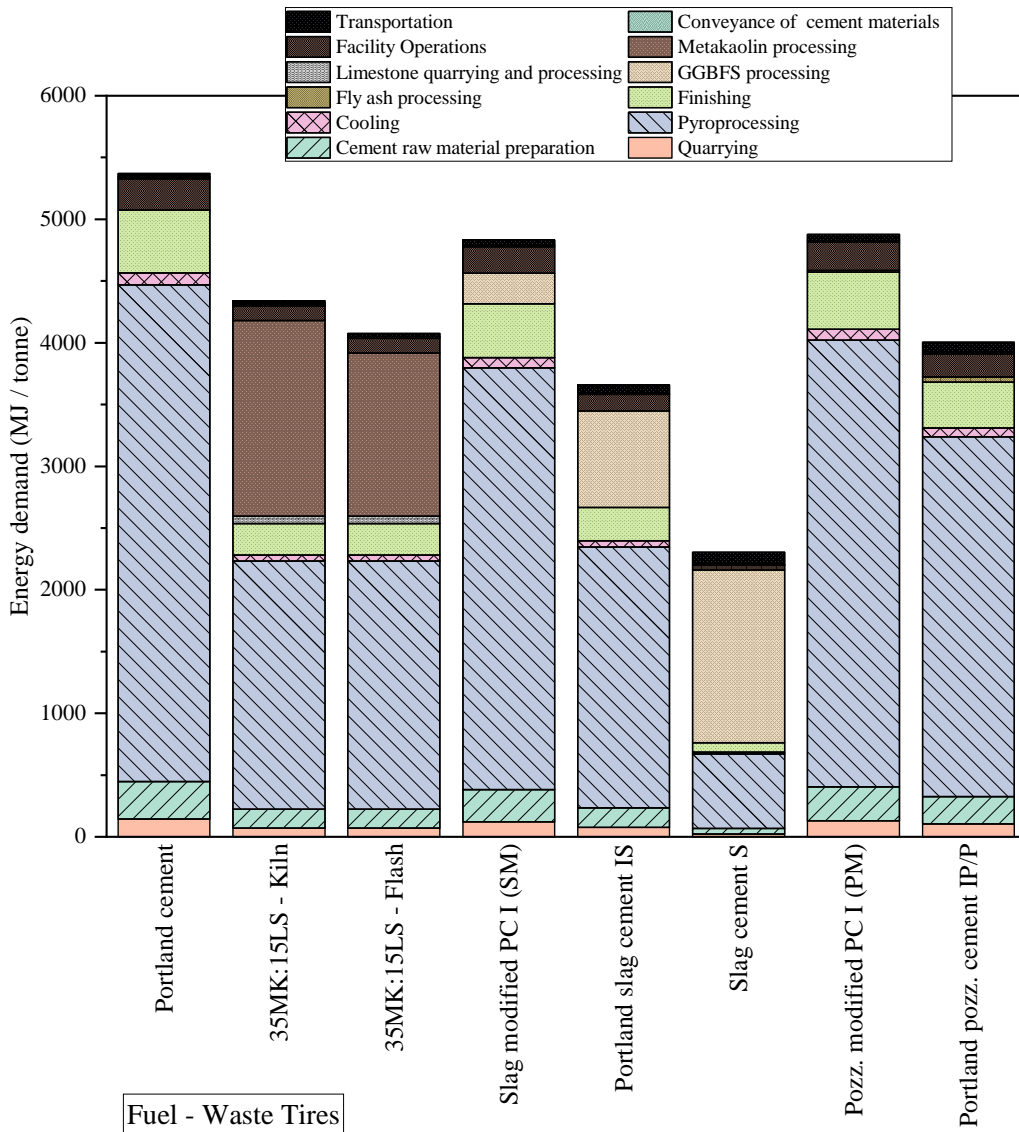
Changes in fuel mix for calcination and pyroprocessing could lead to savings in energy demand and lower GHG emissions from binder production. Figure 6.3 and Figure 6.4 show the influence of changing the fuel mix for calcination and clinker production in the GWP and energy demand of the blended cements reviewed in Chapter 5. As noted in Section 6.1.1, utilizing waste tires as the main fuel for metakaolin calcination and clinker pyroprocessing causes a reduction of 5% to 10% in the GWP and less than 1% reduction in the energy demand. For binders with little process-based

CO<sub>2</sub> emissions (e.g., slag cement), switching to a waste fuel only reduces GHG emissions by 5%. Such binders contain higher replacement ratios of clinker with SCMs that do not need to be subjected to thermal treatment nor do they release significant amounts of CO<sub>2</sub> during the process. Conversely, binders with higher process-based CO<sub>2</sub> emissions and whose SCM content requires thermal activation benefit from the use of waste fuels in order to reduce the overall fossil energy demand and GHG intensity. It is worth noting that even when including these variations of fuel mix used during calcination of metakaolin and the pyroprocessing of clinker, the slag cements and the cements with metakaolin and limestone remain the blended cements with the lowest GWP and energy demand. For blended cements with metakaolin and limestone, further reductions in GHG emissions and energy demand could be achieved with changes in the efficiency of the calcination equipment (i.e., dry rotary kiln) for the best available technology (i.e., flash calciner). Considering the use of waste tires as fuel for calcination and pyroprocessing, a reduction of 4% in the GHG emissions and 6% in the energy demand of these blended cements (i.e., MK:LS cements) is achieved when using a flash calciner for metakaolin's thermal treatment. It is important to highlight those factories that produce clinker by means of wet processing tend to use more waste fuel to control their fuel cost and increase their competitiveness against other cement plants with better and more efficient technologies. This could lead to different results in the overall assessment of GHG emissions and energy demand for regions in the world that still maintain active wet kilns in their cement plants. Because all cement plants in California utilize dry rotary kilns with preheaters and precalciner, the analysis is not included herein.

Finally, transport distances have less influence in these binders since their GHG emissions and energy demand are highly related to the combustion of fuels and the calcination and clinkerization processes. Not included in this work is the consideration of other emissions that could be relevant when assessing the impact to human health and the evaluation and control of criteria and toxic air pollutants (e.g., NO<sub>x</sub>, CO, acetaldehyde, benzene, formaldehyde, etc.) that generate during the burning process of tires.



**Figure 6.3** – Influence of fuel mix input on the GWP of commercial blended cements and cement with metakaolin and limestone. Cements containing metakaolin considered two calcination technologies (i.e., dry rotary kiln and flash calciner). Values are compared with the GHG emissions from portland cement production. All the scenarios are modeled in California with waste tires as the fuel mix used in rotary kilns; Kiln = dry rotary kiln; Flash = flash calciner.



**Figure 6.4** – Influence of fuel mix input on the energy demand of commercial blended cements and cement with metakaolin and limestone. Cements containing metakaolin considered two calcination technologies (i.e., dry rotary kiln and flash calciner). Values are compared with the energy demand from portland cement production. All the scenarios are modeled in California with waste tires as the fuel mix used in rotary kilns; Kiln = dry rotary kiln; Flash = flash calciner.

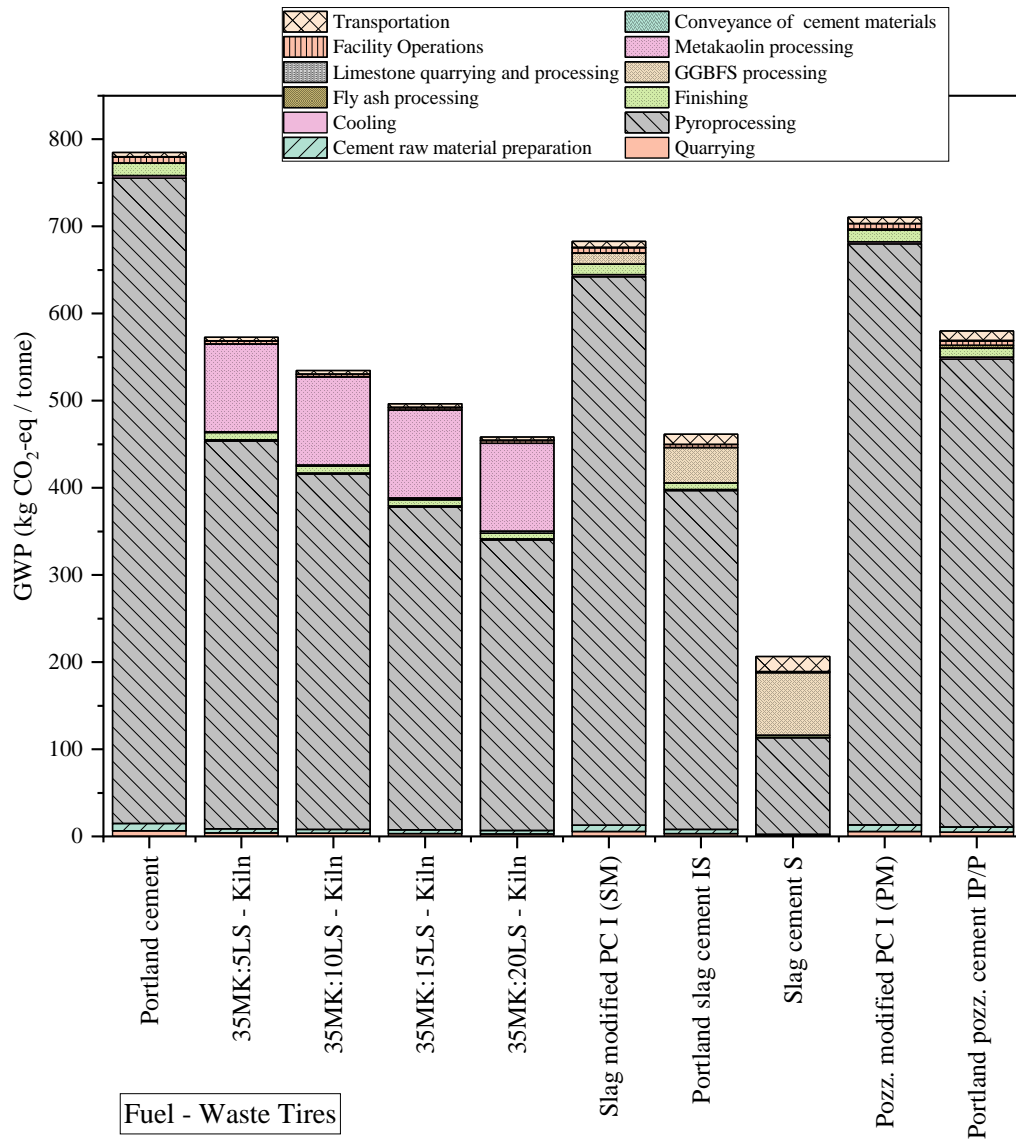
### 6.1.3 Influence of the Total Replacement Ratio of Metakaolin and Limestone on the GWP and Energy Demand of Blended Cements in California

The formulation of ternary cement blends composed of portland cement, metakaolin, and limestone is another variable that should be explored to assess how different formulations compete with portland cement and with other commercially available blended cements in California. For this scenario, all formulations of portland cement and blended cements studied in Chapter 5 were

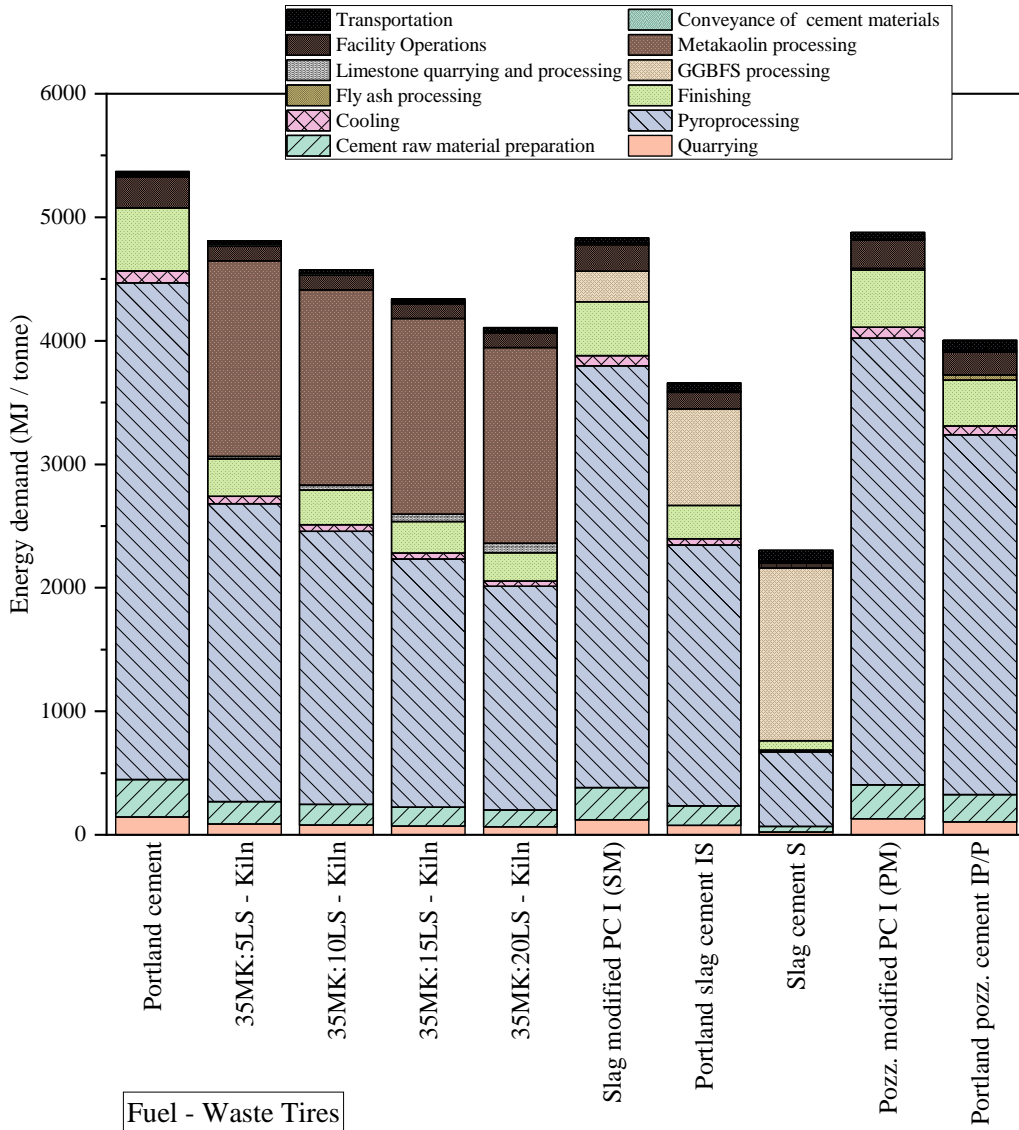
modeled with a fuel mix composed of 100% waste tires and their GWP and energy demand are detailed in Figure 6.5 and Figure 6.6, respectively.

Results indicate that increasing the content of limestone to further reduce the clinker-to-cement ratio reduces the GWP and energy demand of cement blends made of clinker, metakaolin, and limestone. For the cements containing metakaolin and limestone, an overall increase in SCMs by 25% (i.e., 40% replacement vs. 50% replacement or 35MK:5LS vs. 35MK:15LS) resulted in 13% reduction in GHG emissions and 10% reduction in energy demand. A maximum increase of SCMs by 37.5% (i.e., 35MK:5LS vs. 35MK:20LS) resulted in a 20% reduction in GHG emissions and 15% reduction in energy demand. In addition, smaller yet meaningful reductions are achieved when increasing the percentage by mass of limestone from 5% to 10% (i.e., 35MK:5LS vs 35MK:10LS) from which GHG emissions and energy demand are reduced by 7% and 5% respectively. Compared to other cement systems (e.g., blended cements containing slag or fly ash), cements with metakaolin and limestone do still offer the lowest GWP and energy demand by mass basis. The latter are only outperformed by portland slag cements (IS) and slag cement (S) whose clinker substitution ratios correspond of 47.5% and 85%.

As previously mentioned, the GHG emissions and energy demand obtained correspond to those by unit mass of each blended cement and portland cement investigated in Chapters 5 and 6 (i.e., kg CO<sub>2-eq</sub>/tonne and MJ/tonne) and do not consider the structural capacity (i.e., technical performance) of these cements in plain and reinforced concrete applications. Determination of GWP and energy demand is based on specific model parameters, location of raw materials and processing, and energy used, hence results could vary depending on the variation of such inputs.



**Figure 6.5** – Influence of total replacement ratio on the GWP of cements with metakaolin and limestone. Values are compared with the GHG emissions from portland cement production and commercial blended cements. All the scenarios are modeled in California with waste tires as the fuel mix used in rotary kilns.



**Figure 6.6** – Influence of total replacement ratio on the energy demand of cements with metakaolin and limestone. Values are compared with the energy demand from portland cement production and commercial blended cements. All the scenarios are modeled in California with waste tires as the fuel mix used in rotary kilns.

## 6.2 Review of Inventory Data Quality and Data Gaps

Data quality assessment is important in any life-cycle assessment to ensure that the study is using appropriate types of data and that the data match the needs of the study [2]. In this section, the evaluation of the quality of the data used in the development of the MKC-Tool is approached qualitatively following the Pedigree Matrix developed by Weidema et al [145]. The expected effects of various types of uncertainty and variability of data are described in the pedigree matrix shown in Table 6.1.

**Table 6.1** - Qualitative assessment of uncertainty in LCI data via data quality indicators following the Pedigree Matrix Approach with corresponding scoring indicators.

| <b>Indicator Category</b>         | <b>Uncertainty Assessment</b>  | <b>Indicator Score</b> |
|-----------------------------------|--|------------------------|
| Reliability                       | All processes relevant to the production of metakaolin for its use as SCMs in cement blends and concrete are closely related to clinker production, thus the data representative of clinker production has been used when primary data for metakaolin production were not available. Primary data were used when available. However, the user should be aware that the manufacturing maturity of metakaolin used as a SCM is incipient at industrial scale but the material itself has been traditionally used in long-studied processes in other industrial applications that require similar preparation and transformation of the raw material as shown herein. | 2                      |
| Completeness                      | To the best of the author’s knowledge, all processes included effects of direct and indirect production (e.g., upstream emissions). Therefore, cutoff uncertainty is considered to be low.   | 2                      |
| Temporal                          | Primary data of metakaolin production were collected from the year 2019. Secondary data on similar thermal treatment processes, namely, clinker production, were collected from peer-reviewed studies and databases for the years 1995-2020. The user should be aware that cement manufacturing processes have not changed drastically in the last two decades, hence the data are still chosen as the basis for the processes in the study.   | 3                      |
| Geographical                      | Life-cycle inventory data including electricity related emissions, fuel combustion related emissions, and emissions derived from freight transportation are based on databases and published literature relevant to North America and Europe. Lack of regional data outside these regions is unavailable at the time this study has been developed. However, the production conditions and energy requirements for metakaolin production in other areas are judged to be relatively similar.   | 3                      |
| Further technological correlation | Representativeness: Due to the incipient maturity of metakaolin production at industrial scale for its use as supplementary cementitious material in blended cements, fuel and electricity inputs are approximated from cement and clinker processing LCI available for the U.S. and worldwide.  | 4                      |



|  |   |  |
|--|---|--|
|  | <p>Data on cement and clinker production is aggregated into averages and normalized per unit of mass of cement produced. It is expected that the maturity of the manufacturing process and its worldwide application at industrial scale within the next decade will produce more reliable data to feed the tool. It must be emphasized that the tool’s data and methods are of the state of the art in the life-cycle assessment of this material used as SCMs in cement blends.</p> |  |
|--|---|--|

**6.2.1 Other Considerations Relevant to the Assessment of Data Quality**

Higher uncertainty is intrinsically connected to existing data gaps in LCAs of emerging technologies due to the lack of knowledge at the initial phases of a product development (i.e., R&D phase). This is the case of metakaolin production at industrial scale for use as an SCM in blended cements made with clinker. In many cases, the primary data for key processes were not available. Hence, the results are considered estimates and not measurements per se. On that account, when secondary data are used, accurate referencing has been included for all the data collected to build the life-cycle inventory for the MKC-Tool. Consequently, data are unrounded, but are considered to be accurate to no more than one significant digit.

Emissions to air mainly come from the gases released through the combustion of fuels during the pyroprocessing of metakaolin. Because the calcination of metakaolin consumes approximately 79% of the energy demand throughout the entire manufacturing process, data on life-cycle inventory of gas emissions heavily rely on the quality of the data on fuel consumption. Particulate matter (PM) emissions are attained due to PM control devices used within the manufacturing process. The majority of uncontrolled PM release occurs during quarrying of the raw material and transportation to the manufacturing facility. Emissions from diesel-fueled vehicles used for transportation of materials within the system boundary are calculated from peer-reviewed studies that are compatible with the geospatial and temporal scope of this study [115, 116, 146].

Lastly, effects on the methodology chosen to calculate the global warming potential of metakaolin production (i.e., TRACI 2.1[137]) is valid for application in North America. Changing the impact assessment methodology (e.g., GWP 20 years) would not drastically change the results given that these changes would be marked mostly in how methane is evaluated. Methane is not the most important gas released during cement’s production as it is in other industries and economic sectors such as agriculture. Direct CO<sub>2</sub> emissions from cement’s production account for 98-99% of the total GHG emissions in cement plants in CA [147] and direct methane emissions accounted for 2% of total GWP according to the case scenarios evaluated in Chapter 5.

# Chapter 7 – Conclusions and Future Research

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## 7.1 Research Significance

Concrete plays a fundamental role in societies' development by helping create infrastructure and thus boosting the economy. Approximately 25 billion tonnes of concrete and about 4 billion tonnes of cement (concrete's most GHG-intensive ingredient) are produced yearly worldwide. During cement production, approximately 0.9 tons of CO<sub>2</sub> are released into the atmosphere for each ton of cement produced anywhere in the world. These emissions are mainly from the decarbonation of limestone, and are considered to be the largest non-combustion source of CO<sub>2</sub> emissions from industrial production [148]. Considering the importance of climate change, development of green cements is of utmost importance in the advancement of sustainable construction materials. Decarbonizing concrete's life cycle requires special attention to the mitigation strategies that reduce the carbon footprint at the cement level. Multiple strategies have been put in place and continue to be studied (e.g., [148] and [149]). Those which aim to reduce the fraction of clinker in cement are the most reliable ones when considering their ready application in emerging economies where the demand for construction materials— especially cement and concrete— is expected to increase in the next decades.

To satisfy the ever-growing demand for cement-based materials while at the same time focusing on mitigating cement's environmental issues, a careful assessment of these materials' life-cycle impacts on global warming should be performed. In addition, the use of supplementary cementitious materials (SCMs) as partial replacement of clinker in cement should be the focus of attention in the short and medium term to help in the reduction of these impacts and to achieve global targets of emissions reduction. SCMs such as calcined clay and limestone have been identified to be available in the quantities we globally need to provide a sustainable decrease of the clinker-to-cement ratio without compromising cement's and concrete's performance. However, questions such as *What is our reference point for baseline performance of cement-based materials? What is the range of embodied carbon we could expect in this category? How does this particular supplementary cementitious material stack up against this reference point, and against the rest of the potential options?* remain the focus of attention in this research field.

This dissertation focuses on answering these questions by looking into calcined clay as the main supplementary cementitious material to be used as partial replacement of clinker in cement. To this extent, an Excel-based life-cycle assessment tool, the MKC-Tool, has been developed to evaluate metakaolin's life-cycle impacts including (1) global warming potential for air emissions – 100 year, (2) acidification potentials for air emissions, (3) human health particulate potentials for air emissions, (4) eutrophication potentials for air emissions, (5) ozone depletion potentials for air emissions, (6) smog formation potentials for air emissions, (7) freshwater ecotoxicity potentials for urban air emissions, (8) human health cancer potentials for urban air emissions, (9) human health non-cancer potentials for urban air emissions, and (10) fossil fuel depletion from cradle to gate. Results from the tool can be used and included as part of a wider assessment of cement-based materials and their applications. Emphasis on the global warming potential (GWP) is given since the emissions derived from the manufacturing of metakaolin are considered to contribute in a major capacity to the potential cause of climate change. Data on GWP and other environmental impacts resulting from metakaolin's production and use as a supplementary cementitious material have previously relied on average values and data adopted from similar production processes. A

review of previously published studies has proved the weaknesses of life-cycle assessments of metakaolin production. Current LCAs of metakaolin production and use as a supplementary cementitious material in binary and ternary cement blends is limited to emission factors, heating values of fuels, processes linked with extraction of raw materials and fuels, transportation, and electricity based on Ecoinvent database and adapted to local conditions. While this approximation is valid for conducting a screening LCA, more accurate life-cycle inventory data are needed to compare environmental impacts of different cement-based materials. The methods and formulations used at the level of the MKC-Tool are needed to achieve a more robust model and render better and more reliable results. Furthermore, the life-cycle inventory of metakaolin manufacturing process described herein has been carried out taking into consideration the ISO standards 14040 and 14044. These data are used in the MKC-Tool to calculate the LCA of metakaolin production and further used to perform life-cycle assessments of blended cements containing metakaolin as a supplementary cementitious material.

The MKC-Tool has been designed to perform LCAs involving metakaolin used as SCM in concrete or as a pozzolanic addition to blended cements. The main goals are to (1) identify the hotspots or activities with the highest emissions throughout the manufacturing process, and (2) in support of comparing multiple cement-based materials and concretes made with 100% portland cement and/or other cementitious or pozzolanic materials. The MKC-Tool is created to incorporate sustainability into decision making as it helps the user to think broadly about the types of cements that could potentially be used in different projects and their overall environmental impacts.

Experimental testing was another focus of this dissertation in order to study the effect of varying metakaolin to limestone ratios (i.e., 35% by weight of binder of metakaolin and 5%, 10%, 15%, and 20% by weight of binder of limestone) in the mechanical and durability performance of ternary blends made of a combination of portland cement, metakaolin, and limestone. In addition, the effect of the quality of the clay used as SCMs in the performance of mortars and concretes was of main interest. High purity metakaolin (calcined kaolinite mineral content  $\geq 90\%$ ) in combination with limestone has proven to perform very similarly to portland cement mixes with equal water-cement ratio. However, deposits of suitable clays worldwide present variations in their content of kaolinite mineral. Therefore, the experimental plan included three clays with varying kaolin content (i.e., 43%, 82%, and 98%). For low-grade calcined clays (i.e., calcined kaolinite content of 43%), comparable values to those from PC mortars were achieved for co-substitution of 35% metakaolin and 5-10% of limestone (i.e., 35MK with 5LS, 10LS) after only 3 days, which demonstrates the feasibility of using a wider range of calcined clays with varying calcined kaolinite content even at higher coupled substitution ratios with limestone (total substitution of 40% and 45% of clinker).

## **7.2 Future Research and Areas of Improvement**

Decarbonization of the cement and concrete industries continue to be one of the top priorities on the path to a carbon-neutral economy and reductions of the effects of global warming and its damages to societies and ecosystems. To sufficiently appreciate the environmental burden of construction materials, the use of life-cycle assessment tools is required. Life-cycle assessments help to identify the potential strategies to reduce greenhouse gas and other emissions associated with the production of cement-based materials. To this extent, the MKC-Tool is useful in

evaluating the emissions derived from the production of metakaolin as a supplementary cementitious material to be used in blended cements composed of clinker, metakaolin, and limestone. However, we should note that the nature of life-cycle assessments of emerging technologies is subject to uncertainties as the product and its manufacturing process mature and become more widespread. Accordingly, one must note the following potential areas of improvement for future development of the MKC-LCA Tool:

- The tool currently allows for the quantification of water consumption throughout the different production phases. However, the carbon footprint of water usage is not currently included in the tool. There is high uncertainty in the impacts of water consumption and withdrawal during the production of metakaolin given the incipient nature of the process at industrial scale and the lack of available primary data. This aspect would be included in the tool as the production process of metakaolin and its use as SCM in ternary blends of cement with limestone matures and accurate data become more readily available.
- Expanding the system boundary and scope of the MKC-Tool to include *gate-to-gate* or *cradle-to-grave* and end-of-life emissions would allow one to calculate the environmental impacts of metakaolin production in a more comprehensive manner as this assessment would account for the entire life cycle of the material. This is of special interest when including the emissions from metakaolin production in the overall life-cycle assessment of cement blends, concretes made with these blends, as well as structural members and entire buildings. Other important aspects such as durability and mechanical performance could be better analyzed when including those impacts and the considerations of these materials' service lives. These aspects are strongly related to the current functional unit of analysis within the tool (i.e., impacts by unit of mass) which allows one to evaluate the emissions of metakaolin production up to the gate of the production facility so that results obtained could be easily incorporated into cement and concrete LCAs. However, functional units based on function (e.g., mechanical performance, durability, service life, etc.) could allow for a holistic evaluation of the life-cycle impacts of these construction materials and would let the user incorporate sustainability into decision making.
- It is important to understand that values for thermal energy input could vary depending on the type, grade, size and particle distribution of the feed material (raw kaolin). Because the technology used for calcination and its energy efficiency as well as the fuel used to feed the system play a great role in the thermal energy consumed during the process, this aspect should be considered within the tool in the future. Accounting for different grades of kaolin and their effect in residency time and calcination temperature as well as total raw material input to produce a specific amount of metakaolin as final product should be explored. The MKC-LCA Tool only accounts for a fixed raw clay-to-metakaolin ratio, calculated based on the average value reported in the literature.
- Due to lack of primary data, energy values corresponding to raw kaolin processing before calcination (drying and pulverizing) are adapted from similar processing of cement raw materials. In addition, when the fuel mix for metakaolin calcination is not known by the user, the U.S. average fuel mix for clinker pyroprocessing is used as the average fuel mix for clay calcination. As these values are approximates, data from kaolin processing would yield a more accurate evaluation of environmental impacts.

- In addition, regional and technological inventory data in metakaolin manufacturing would render more accurate results in terms of the total emissions produced during this material's production. Emission factors and energy consumption are currently based on data modeled mainly in North America and Europe; hence the results obtained from this tool should be carefully interpreted when evaluating emissions produced in other regions of the world. As data become available in the future, the tool would include life-cycle inventory data specific to the region of interest by the user. In all, working closely with cement manufacturers would help facilitate the input of primary life-cycle inventory data into the tool to develop more reliable and robust results that are regionally focused. The tool would be improved by a future data collection process when more data become available as the technology matures over time.
- Life-cycle inventory emissions associated with transportation of materials within the system boundary are based on LCI data published for typical vehicles used for freight transportation in North America [115, 150] and do not consider other regions. Even though vehicles covered in these studies are considered representative of the technology and use within the cement production sector, considerations such as model, utilization (full or not full), and capacity of vehicles used in emerging countries which are usually based on older, more polluting models might render different results. The tool should include and consider these scenarios of freight transportation LCAs that cover other regions and countries.
- When using LCA in support of decision making, one should consider the performance of each alternative under study. In this context, the development of mechanical properties of mortars and concretes made with ternary blends of portland cement, metakaolin, and limestone may be different from those made with traditional portland cement. This brings up the question of how to normalize the environmental impacts for a given mechanical property. A broader overview of these cement-based materials' environmental impacts would be possible when accounting for parameters such as age of the composite, compressive strength, quality and grade of the calcined clay, etc. Moreover, while proper mechanical strength is necessary, other properties may be more appropriate for specific exposure of the structure. Therefore, durability parameters should be introduced in the assessment. These are not currently included in the tool due to lack of a standard protocol.
- The inclusion and calculation of other methodologies for environmental impact assessment calculations (e.g., ReCiPE 2016, IMPACT 2002) would extend the environmental profile evaluation of this material and would allow one to better understand its performance when combined with cement and limestone in cement and concrete applications. Additionally, the results obtained in the MKC-Tool could be further implemented in designing sustainable concrete mixtures by means of machine learning. Artificial intelligence techniques that combine environmental analysis with performance of concrete and the use of SCMs in order to reduce cement's and concrete's carbon footprint will benefit from the outputs of the MKC-tool by optimizing mix designs based on raw materials' availability, cost, and performance goals (e.g., carbon footprint, compressive strength, corrosion resistance, service life, energy use).
- In the present work, only portland cement clinker was used in the analysis of ternary cement blends with metakaolin and limestone. However, new generation of cements with reduced carbon footprint (e.g., belite cements, sulfoaluminate cements) could further reduce the

overall environmental impact of cement when used in conjunction with metakaolin and limestone. Hence the interactions with these alternative binders and coupled substitutions of metakaolin and limestone should be further investigated. A related point to consider is the source of calcium carbonates. In this dissertation, only limestone in the form of calcite was used. However, technologies of carbon sequestration developed in recent years can produce various polymorphous calcium carbonates (e.g., vaterite, aragonite, amorphous calcium carbonates) and it is also important to study their interactions with calcined clays in blended cements. Additional aspects to consider are (1) the interaction of these cements with fibers and their contribution to controlling the size of the crack opening in fiber-reinforced concrete applications, (2) optimization of the ternary blend cements with varying metakaolin content, (3) the role of high curing temperatures in the kinetics of hydration of these ternary blends as commonly done in precast concrete applications, as well as other properties of concrete at early age such as autogenous and drying shrinkage.

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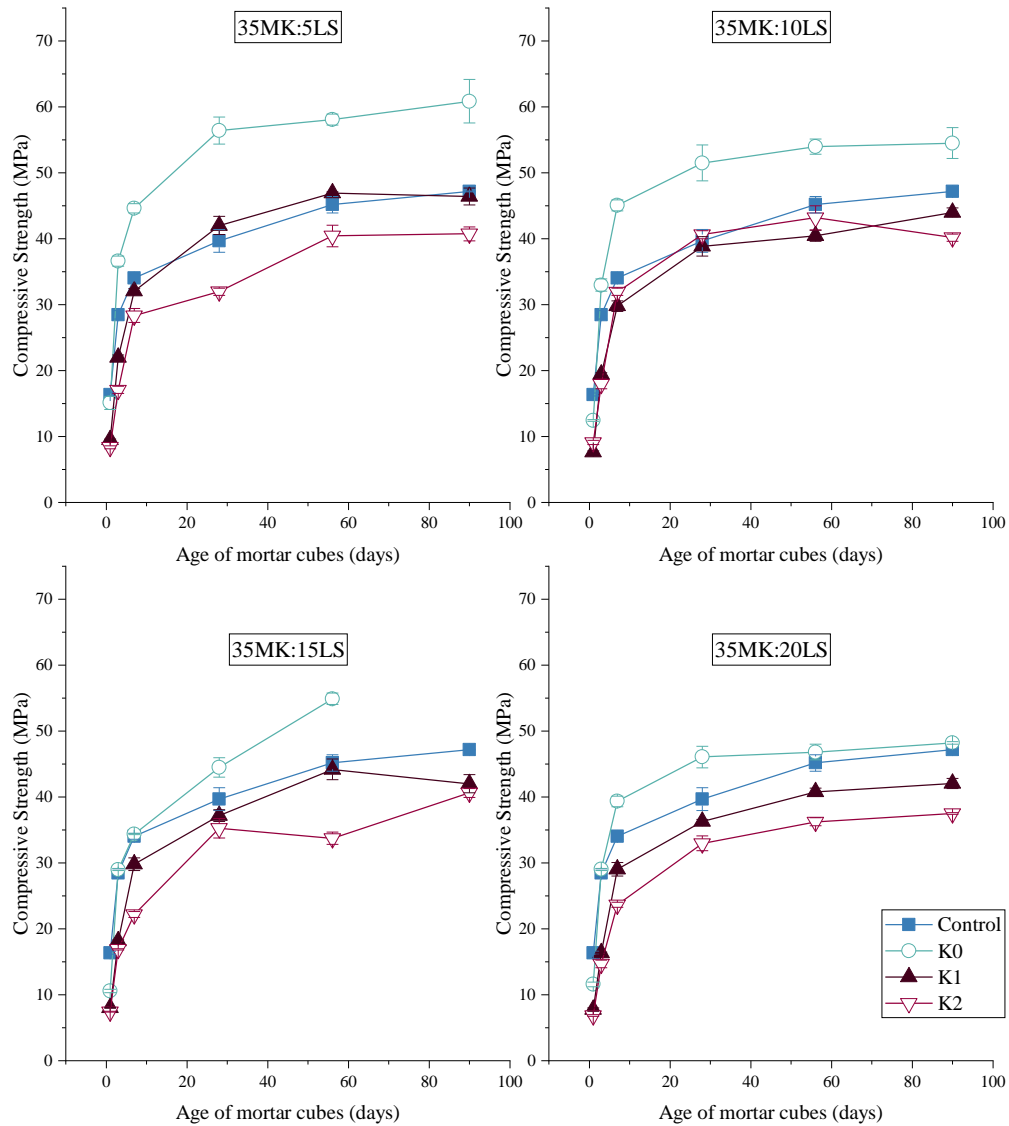
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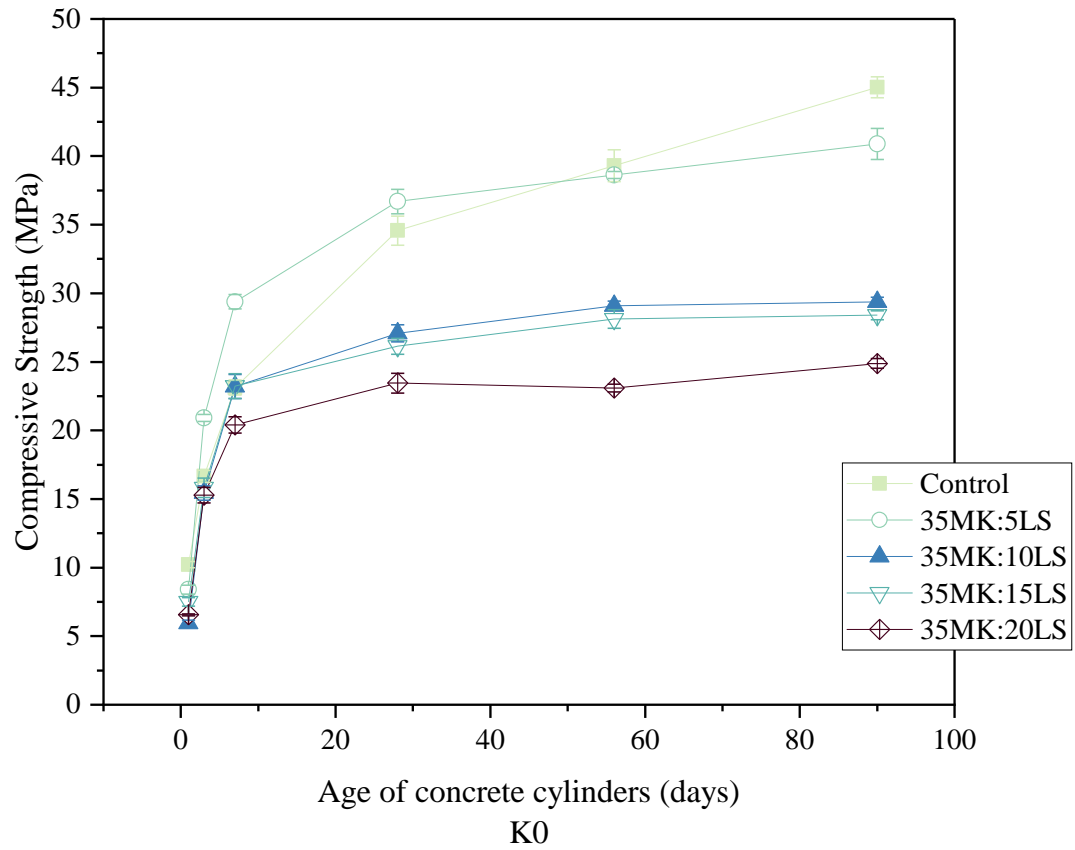
# Appendix

## Appendix A: Experimental Results



**Figure A. 1** - Evolution of compressive strength of mortar mixes with 35% metakaolin replacement of varying calcined kaolinite content and different limestone content (i.e., 5%, 10%, 15%, and 20%). The *Control* mix with 100% portland cement is also displayed.





**Figure A. 2** - Evolution of compressive strength of concrete mixes with 35% metakaolin replacement and varying limestone content (i.e., 5%, 10%, 15%, and 20%). The *Control* mix with 100% portland cement is also displayed.

## Appendix B: MKC-Tool LCI Data

Table A. 1 – LCI Data for fuel pre-combustion. Adapted from [110]

|  |                | Bituminous coal | Lignite coal | Distillate (Diesel) fuel oil | Gasoline | Kerosene | LPG      | Petroleum coke | Residual (heavy) fuel oil | Natural gas       | Nuclear  |
|--|----------------|-----------------|--------------|------------------------------|----------|----------|----------|----------------|---------------------------|-------------------|----------|
| Unit                                   |                | kg              | kg           | l                            | l        | l        | l        | kg             | l                         | m <sup>3</sup>    | kg       |
| <b>HHV (MJ/unit)</b>                   |                | 27.91           | 15.12        | 38.32                        | 27.87    | 27.9     | 25.4     | 35.7           | 41.72                     | 38.23             | 451,405  |
| <b>Inputs</b>                          | Units          |                 |              |                              |          |          |          |                |                           |                   |          |
| <b>Bituminous Coal</b>                 | kg             | 1.16E-02        | 1.40E-02     | 4.21E-02                     | 3.58E-02 | 3.92E-02 | 2.63E-02 | -              | 4.58E-02                  | 1.21E-02          | 1.03E+03 |
| <b>Lignite Coal</b>                    | kg             | 2.40E-05        | 1.66E-03     | 3.91E-03                     | 3.33E-03 | 3.65E-03 | 2.44E-03 | -              | 4.26E-03                  | 1.12E-03          | 9.33E+01 |
| <b>Distillate oil</b>                  | l              | 1.62E-02        | 2.10E-03     | 6.11E-03                     | 5.21E-03 | 5.70E-03 | 3.82E-03 | -              | 6.66E-03                  | 1.77E-03          | 3.97E+01 |
| <b>Gasoline</b>                        | l              | 8.63E-04        | 1.45E-03     | 7.35E-04                     | 6.26E-04 | 6.85E-04 | 4.59E-04 | -              | 8.00E-04                  | 6.13E-04          | 1.36E+00 |
| <b>Kerosene</b>                        | l              | 0.00E+00        | 0.00E+00     | 0.00E+00                     | 0.00E+00 | 0.00E+00 | 0.00E+00 | -              | 0.00E+00                  | 0.00E+00          | 0.00E+00 |
| <b>LPG</b>                             | l              | 2.19E-05        | 2.30E-05     | 1.06E-03                     | 9.06E-04 | 9.91E-04 | 6.64E-04 | -              | 1.16E-03                  | 4.65E-06          | 1.21E-01 |
| <b>Residual oil</b>                    | l              | 3.09E-03        | 1.65E-02     | 4.92E-02                     | 4.19E-02 | 4.59E-02 | 3.07E-02 | -              | 5.35E-02                  | 1.35E-03          | 4.35E+01 |
| <b>Natural Gas</b>                     | m <sup>3</sup> | 3.66E-03        | 7.35E-02     | 5.56E-02                     | 4.74E-02 | 5.19E-02 | 3.47E-02 | -              | 6.05E-02                  | 7.43E-02          | 4.36E+02 |
| <b>Nuclear</b>                         | kg             | 2.90E-08        | 3.83E-08     | 1.24E-07                     | 1.05E-07 | 1.15E-07 | 7.73E-08 | -              | 1.35E-07                  | 3.30E-08          | 2.74E-03 |
| <b>Wood (or other Biomass)</b>         | MJ             | 1.31E-02        | 1.73E-02     | 5.59E-02                     | 4.77E-02 | 5.22E-02 | 3.50E-02 | -              | 6.09E-02                  | 1.49E-02          | 1.24E+03 |
| <b>Hydro</b>                           | MJ             | 1.25E-02        | 1.64E-02     | 5.31E-02                     | 4.53E-02 | 4.95E-02 | 3.32E-02 | -              | 5.78E-02                  | 1.42E-02          | 1.18E+03 |
| <b>Pre-combustion energy use unit</b>  |                | MJ/kg           | MJ/kg        | MJ/l                         | MJ/l     | MJ/l     | MJ/l     | MJ/kg          | MJ/l                      | MJ/m <sup>3</sup> | MJ/kg    |
| <b>Pre-combustion energy use value</b> |                | 1.28E+00        | 4.09E+00     | 5.86E+00                     | 4.99E+00 | 5.46E+00 | 3.66E+00 | -              | 6.37E+00                  | 3.38E+00          | 5.39E+04 |

|                                    |       | Bituminous coal | Lignite coal | Distillate (Diesel) fuel oil | Gasoline | Kerosene | LPG      | Petroleum coke | Residual (heavy) fuel oil | Natural gas | Nuclear  |
|------------------------------------|-------|-----------------|--------------|------------------------------|----------|----------|----------|----------------|---------------------------|-------------|----------|
| <b>Water consumption range</b>     | l/GJ  | 5-70            | 5-70         | 28-72                        | 28-72    | 28-72    | 28-72    | 28-72          | 28-72                     | 7.00E+00    | 29-51    |
| <b>Water consumption (average)</b> | l/GJ  | 3.75E+01        | 3.75E+01     | 5.00E+01                     | 5.00E+01 | 5.00E+01 | 5.00E+01 | 5.00E+01       | 5.00E+01                  | 7.00E+00    | 4.00E+01 |
| <b>Water consumption</b>           | kg    | 1.05E+00        | 5.67E-01     | 1.92E+00                     | 1.39E+00 | 1.40E+00 | 1.27E+00 | 1.79E+00       | 2.09E+00                  | 2.68E-01    | 1.81E+04 |
| <b>Outputs</b>                     | Units |                 |              |                              |          |          |          |                |                           |             |          |
| <b>Solid waste</b>                 | kg    | 2.21E-01        | 5.77E-03     | 4.64E-02                     | 3.95E-02 | 4.32E-02 | 2.90E-02 | -              | 5.05E-02                  | 2.57E-02    | 5.26E+03 |
| <b>Air emissions</b>               |       |                 |              |                              |          |          |          |                |                           |             |          |
| <b>CO<sub>2</sub>-eq</b>           | kg    | 1.85E-01        | 1.37E-01     | 4.92E-01                     | 4.19E-01 | 4.59E-01 | 3.07E-01 | -              | 5.35E-01                  | 4.46E-01    | 3.86E+03 |
| <b>Sb</b>                          | kg    | 1.43E-10        | -            | 5.25E-10                     | 4.47E-10 | 4.89E-10 | 3.28E-10 | -              | 5.71E-10                  | 1.49E-10    | 1.25E-05 |
| <b>As</b>                          | kg    | 3.72E-09        | -            | 1.44E-08                     | 1.23E-08 | 1.34E-08 | 9.00E-09 | -              | 1.57E-08                  | 3.25E-09    | 2.45E-04 |
| <b>Be</b>                          | kg    | 5.63E-10        | -            | 6.84E-10                     | 5.83E-10 | 6.38E-10 | 4.28E-10 | -              | 7.45E-10                  | 2.19E-10    | 1.38E-05 |
| <b>Cd</b>                          | kg    | 9.69E-10        | -            | 3.59E-09                     | 3.06E-09 | 3.35E-09 | 2.25E-09 | -              | 3.91E-09                  | 1.48E-09    | 4.13E-05 |
| <b>CO<sub>2</sub></b>              | kg    | 9.43E-02        | 1.07E-01     | 3.93E-01                     | 3.35E-01 | 3.67E-01 | 2.46E-01 | -              | 4.28E-01                  | 1.86E-01    | 3.63E+03 |
| <b>CO</b>                          | kg    | 4.34E-04        | 4.73E-04     | 1.27E-02                     | 1.08E-02 | 1.18E-02 | 7.91E-03 | -              | 1.38E-02                  | 2.18E-04    | 2.90E+00 |
| <b>Cr</b>                          | kg    | 2.53E-09        | -            | 1.04E-08                     | 8.84E-09 | 9.68E-09 | 6.49E-09 | -              | 1.13E-08                  | 3.27E-09    | 1.67E-04 |
| <b>Co</b>                          | kg    | 2.77E-09        | -            | 2.24E-08                     | 1.91E-08 | 2.09E-08 | 1.40E-08 | -              | 2.44E-08                  | 1.66E-09    | 8.73E-05 |
| <b>Cu</b>                          | kg    | 8.30E-10        | -            | 1.67E-10                     | 1.43E-10 | 1.56E-10 | 1.05E-10 | -              | 1.82E-10                  | 1.22E-10    | 3.06E-06 |
| <b>CH<sub>2</sub>O</b>             | kg    | 5.08E-08        | -            | 2.67E-07                     | 2.28E-07 | 2.49E-07 | 1.67E-07 | -              | 2.91E-07                  | 3.01E-07    | 2.36E-03 |
| <b>Pb</b>                          | kg    | 7.30E-09        | 3.13E-08     | 1.62E-08                     | 1.38E-08 | 1.51E-08 | 1.01E-08 | -              | 1.76E-08                  | 3.86E-09    | 3.04E-04 |
| <b>Mn</b>                          | kg    | 1.04E-08        | -            | 4.42E-08                     | 3.76E-08 | 4.12E-08 | 2.76E-08 | -              | 4.81E-08                  | 1.02E-08    | 7.90E-04 |
| <b>Hg</b>                          | kg    | 1.28E-09        | 1.20E-09     | 2.66E-09                     | 2.26E-09 | 2.48E-09 | 1.66E-09 | -              | 2.89E-09                  | 8.82E-10    | 6.57E-05 |
| <b>CH<sub>4</sub></b>              | kg    | 3.92E-03        | 1.30E-03     | 4.19E-03                     | 3.57E-03 | 3.91E-03 | 2.62E-03 | -              | 4.56E-03                  | 1.13E-02    | 9.09E+00 |
| <b>Ni</b>                          | kg    | 3.19E-08        | -            | 2.89E-07                     | 2.46E-07 | 2.69E-07 | 1.80E-07 | -              | 3.14E-07                  | 1.66E-08    | 5.87E-04 |
| <b>NO<sub>x</sub></b>              | kg    | 7.34E-04        | 3.33E-04     | 3.00E-03                     | 2.56E-03 | 2.80E-03 | 1.88E-03 | -              | 3.27E-03                  | 2.62E-04    | 2.19E+01 |

|                           |    | <b>Bituminous coal</b> | <b>Lignite coal</b> | <b>Distillate (Diesel) fuel oil</b> | <b>Gasoline</b> | <b>Kerosene</b> | <b>LPG</b> | <b>Petroleum coke</b> | <b>Residual (heavy) fuel oil</b> | <b>Natural gas</b> | <b>Nuclear</b> |
|---------------------------|----|------------------------|---------------------|-------------------------------------|-----------------|-----------------|------------|-----------------------|----------------------------------|--------------------|----------------|
| <b>N<sub>2</sub>O</b>     | kg | 1.78E-06               | 1.45E-06            | 7.23E-06                            | 6.16E-06        | 6.74E-06        | 4.52E-06   | -                     | 7.87E-06                         | 3.77E-06           | 8.84E-02       |
| <b>NMVO</b>               | kg | 7.45E-07               | 8.55E-07            | 2.54E-06                            | 2.17E-06        | 2.37E-06        | 1.59E-06   | -                     | 2.77E-06                         | 7.30E-07           | 6.38E-02       |
| <b>PM<sub>10</sub></b>    | kg | 2.01E-05               | 1.01E-05            | 7.70E-05                            | 6.56E-05        | 7.18E-05        | 4.81E-05   | -                     | 8.38E-05                         | 1.31E-05           | 3.84E-01       |
| <b>PM<sub>total</sub></b> | kg | 1.53E-03               | 1.31E-04            | 2.98E-04                            | 2.54E-04        | 2.78E-04        | 1.86E-04   | -                     | 3.25E-04                         | 2.27E-05           | 1.88E+01       |
| <b>Se</b>                 |    | 0.00E+00               | 0.00E+00            | 0.00E+00                            | 0.00E+00        | 0.00E+00        | 0.00E+00   | 0.00E+00              | 0.00E+00                         | 0.00E+00           | 0.00E+00       |
| <b>SO<sub>2</sub></b>     | kg | 2.58E-04               | 4.52E-04            | 1.67E-03                            | 1.43E-03        | 1.56E-03        | 1.05E-03   | -                     | 1.82E-03                         | 1.94E-02           | 7.41E+01       |
| <b>VOC (unspecified)</b>  | kg | 5.05E-05               | -                   | 1.19E-04                            | 1.01E-04        | 1.11E-04        | 7.43E-05   | -                     | 1.29E-04                         | 6.17E-04           | 3.52E-01       |
| <b>Zn</b>                 | kg | 5.53E-10               | -                   | 1.12E-10                            | 9.50E-11        | 1.04E-10        | 6.97E-11   | -                     | 1.21E-10                         | 8.13E-11           | 2.04E-06       |

**Table A. 2** – LCI data of fuel combustion of typical fuels used during calcination. Adapted from [13, 110, 112, 114, 117]

|                                       | <b>Unit</b> | <b>Bituminous coal</b> | <b>Lignite coal</b> | <b>Petroleum coke</b> | <b>Natural gas</b>   | <b>Residual (heavy) fuel oil</b> | <b>Distillate (Diesel) fuel oil</b> | <b>Gasoline</b> |
|---------------------------------------|-------------|------------------------|---------------------|-----------------------|----------------------|----------------------------------|-------------------------------------|-----------------|
| <b>Unit</b>                           |             | <b>kg</b>              | <b>kg</b>           | <b>kg</b>             | <b>m<sup>3</sup></b> | <b>l</b>                         | <b>l</b>                            | <b>l</b>        |
| <b>HHV (MJ per unit)</b>              |             | 27.91                  | 15.12               | 35.7                  | 38.23                | 41.72                            | 38.32                               | 27.87           |
| <b>Density</b>                        | kg/l        | -                      | -                   | 0.8                   | -                    | 0.95                             | 0.84                                | -               |
| <b>Oxidation, O</b>                   | %           | 100                    | 100                 | 100                   | 100                  | 100                              | 100                                 | 100             |
| <b>Elemental Analysis of Fuels</b>    |             |                        |                     |                       |                      |                                  |                                     |                 |
| <b>C (total)</b>                      | %           | 72.25                  | 66.9                | 86.57                 | -                    | 85.7                             | 86.5                                | -               |
| <b>H</b>                              | %           | 4.9                    | 4.7                 | 3.25                  | -                    | 11.2                             | 13.6                                | -               |
| <b>O</b>                              | %           | 9.3                    | 19.04               | -                     | -                    | -                                | -                                   | -               |
| <b>N</b>                              | %           | 1.4                    | 1.3                 | 1.67                  | -                    | 0.37                             | 0.005                               | -               |
| <b>S</b>                              | %           | 1                      | 0.8                 | 5.5                   | -                    | 2.1                              | 0.095                               | -               |
| <b>Chlorine (Cl)</b>                  | %           | -                      | -                   | -                     | -                    | -                                | -                                   | -               |
| <b>Fluorine (F)</b>                   | %           | -                      | -                   | -                     | -                    | -                                | -                                   | -               |
| <b>Ash (solid waste)</b>              | %           | 9                      | 7.3                 | 0.4                   | -                    | -                                | 0.01                                | -               |
| <b>H<sub>2</sub>O</b>                 | %           | 8                      | 33.7                | 6.28                  | -                    | 2                                | 0.05                                | -               |
| <b>Volatiles</b>                      | %           | 32.1                   | 29.2                | 11.18                 | -                    | -                                | -                                   | -               |
| <b>CO<sub>2</sub> per HHV of fuel</b> | kg/MJ       | 9.61E-02               | 1.01E-01            | 9.75E-02              | 5.61E-02             | 7.74E-02                         | 7.41E-02                            | 6.93E-02        |
| <b>CH<sub>4</sub> per HHV of fuel</b> | kg/MJ       | 1.00E-05               | 1.00E-05            | 3.00E-06              | 8.53E-07             | 3.00E-06                         | 3.00E-06                            | 3.00E-06        |
| <b>Solid waste</b>                    | kg          | 9.00E-02               | 7.30E-02            | 4.00E-03              | -                    | -                                | 1.00E-04                            | -               |



|                          | <b>Unit</b> | <b>Bituminous coal</b> | <b>Lignite coal</b> | <b>Petroleum coke</b> | <b>Natural gas</b>   | <b>Residual (heavy) fuel oil</b> | <b>Distillate (Diesel) fuel oil</b> | <b>Gasoline</b> |
|--------------------------|-------------|------------------------|---------------------|-----------------------|----------------------|----------------------------------|-------------------------------------|-----------------|
|                          |             | <b>kg</b>              | <b>kg</b>           | <b>kg</b>             | <b>m<sup>3</sup></b> | <b>l</b>                         | <b>l</b>                            | <b>l</b>        |
| <b>Se</b>                |             | 0.00E+00               | 0.00E+00            | 0.00E+00              | 0.00E+00             | 0.00E+00                         | 0.00E+00                            | 0.00E+00        |
| <b>SO<sub>2</sub></b>    | kg          | 2.00E-02               | 1.60E-02            | 1.55E-02              | -                    | 4.42E-02                         | 2.28E-03                            | 5.01E-04        |
| <b>VOC (unspecified)</b> | kg          | 7.14E-05               | 6.43E-05            | -                     | 8.81E-05             | 1.20E-04                         | 6.23E-06                            | 2.84E-03        |
| <b>Zn</b>                | kg          | -                      | -                   | -                     | 4.65E-07             | 3.42E-06                         | 1.72E-09                            | -               |

**Table A. 3** – LCI data of fuel combustion of waste fuels used during calcination. Adapted from [13, 110, 112, 114, 117]

|                          | <b>Unit</b>  | <b>Waste oil</b> | <b>Waste solvent</b> | <b>Waste tire (whole)</b> | <b>Waste tire (shredded)</b> | <b>Waste paper (cardboard, wood)</b> | <b>Waste plastics</b> | <b>Waste sewage sludge (dry)</b> | <b>Waste (other/non-hazardous)</b> | <b>Waste (other/hazardous)</b> |
|--------------------------|--------------|------------------|----------------------|---------------------------|------------------------------|--------------------------------------|-----------------------|----------------------------------|------------------------------------|--------------------------------|
|                          | <b>Unit</b>  | <b>kg</b>        | <b>kg</b>            | <b>kg</b>                 | <b>kg</b>                    | <b>kg</b>                            | <b>kg</b>             | <b>kg</b>                        | <b>kg</b>                          | <b>kg</b>                      |
| <b>Energy</b>            | <b>MJ/kg</b> | 3.29E+01         | 2.94E+01             | 3.73E+01                  | 3.73E+01                     | 1.48E+01                             | 2.99E+01              | 1.10E+01                         | 1.79E+01                           | 2.98E+01                       |
| <b>Water</b>             | <b>kg</b>    | 0.00E+00         | 0.00E+00             | 0.00E+00                  | 0.00E+00                     | 0.00E+00                             | 0.00E+00              | 0.00E+00                         | 0.00E+00                           | 0.00E+00                       |
| <b>Solid waste</b>       | <b>kg</b>    | 5.22E-02         | 8.50E-02             | 9.08E-02                  | 9.08E-02                     | 6.00E-03                             | 1.02E-01              | 3.80E-01                         | 4.79E-02                           | 1.67E-01                       |
| <b>CO<sub>2</sub>-eq</b> | <b>kg</b>    | 2.44E+00         | 1.66E+00             | 2.62E+00                  | 2.62E+00                     | 1.63E+00                             | 2.10E+00              | 9.91E-01                         | 2.24E+00                           | 1.49E+00                       |
| <b>Sb</b>                | <b>kg</b>    | 5.51E-09         | 0.00E+00             | 0.00E+00                  | 0.00E+00                     | 0.00E+00                             | 0.00E+00              | 0.00E+00                         | 0.00E+00                           | 0.00E+00                       |
| <b>As</b>                | <b>kg</b>    | 2.56E-09         | 3.63E-09             | 6.91E-09                  | 6.91E-09                     | 3.70E-08                             | 8.30E-10              | 5.30E-09                         | 5.60E-09                           | 6.20E-09                       |
| <b>Be</b>                | <b>kg</b>    | 0.00E+00         | 0.00E+00             | 0.00E+00                  | 0.00E+00                     | 0.00E+00                             | 0.00E+00              | 0.00E+00                         | 0.00E+00                           | 0.00E+00                       |
| <b>Cd</b>                | <b>kg</b>    | 3.32E-09         | 3.12E-09             | 1.24E-08                  | 1.24E-08                     | 2.50E-10                             | 9.50E-10              | 1.57E-09                         | 1.83E-09                           | 1.54E-09                       |
| <b>CO<sub>2</sub></b>    | <b>kg</b>    | 2.41E+00         | 1.66E+00             | 3.17E+00                  | 3.17E+00                     | 1.63E+00                             | 2.24E+00              | 9.92E-01                         | 1.28E+03                           | 2.36E+03                       |
| <b>CO</b>                | <b>kg</b>    | 0.00E+00         | 0.00E+00             | 0.00E+00                  | 0.00E+00                     | 0.00E+00                             | 0.00E+00              | 0.00E+00                         | 0.00E+00                           | 0.00E+00                       |
| <b>Cr</b>                | <b>kg</b>    | 1.29E-08         | 8.29E-08             | 2.89E-08                  | 2.89E-08                     | 4.20E-08                             | 8.30E-09              | 7.10E-08                         | 8.23E-09                           | 8.00E-08                       |
| <b>Co</b>                | <b>kg</b>    | 4.72E-09         | 9.54E-09             | 1.77E-08                  | 1.77E-08                     | 1.00E-09                             | 9.38E-09              | 7.33E-09                         | 5.96E-09                           | 1.95E-08                       |
| <b>Cu</b>                | <b>kg</b>    | 7.10E-08         | 1.97E-07             | 7.00E-08                  | 7.00E-08                     | 4.40E-08                             | 1.03E-07              | 3.58E-07                         | 4.76E-08                           | 2.69E-07                       |
| <b>CH<sub>2</sub>O</b>   | <b>kg</b>    | 0.00E+00         | 0.00E+00             | 0.00E+00                  | 0.00E+00                     | 0.00E+00                             | 0.00E+00              | 0.00E+00                         | 0.00E+00                           | 0.00E+00                       |
| <b>Pb</b>                | <b>kg</b>    | 2.53E-08         | 1.45E-07             | 2.14E-08                  | 2.14E-08                     | 7.00E-09                             | 3.79E-08              | 0.00E+00                         | 4.02E-08                           | 1.25E-07                       |
| <b>Mn</b>                | <b>kg</b>    | 1.54E-08         | 1.31E-08             | 1.66E-07                  | 1.66E-07                     | 4.00E-08                             | 4.32E-08              | 3.21E-07                         | 9.50E-09                           | 2.68E-07                       |



|                           | Unit      | Waste oil | Waste solvent | Waste tire (whole) | Waste tire (shredded) | Waste paper (cardboard, wood) | Waste plastics | Waste sewage sludge (dry) | Waste (other/non-hazardous) | Waste (other/hazardous) |
|---------------------------|-----------|-----------|---------------|--------------------|-----------------------|-------------------------------|----------------|---------------------------|-----------------------------|-------------------------|
|                           | Unit      | kg        | kg            | kg                 | kg                    | kg                            | kg             | kg                        | kg                          | kg                      |
| <b>Hg</b>                 | <b>kg</b> | 4.20E-10  | 8.20E-10      | 2.70E-10           | 2.70E-10              | 2.00E-11                      | 2.00E-11       | 8.90E-10                  | 1.83E-08                    | 4.00E-10                |
| <b>CH<sub>4</sub></b>     | <b>kg</b> | 9.88E-04  | 0.00E+00      | 1.06E-04           | 1.06E-04              | 0.00E+00                      | 0.00E+00       | 0.00E+00                  | 0.00E+00                    | 0.00E+00                |
| <b>Ni</b>                 | <b>kg</b> | 1.69E-08  | 4.43E-08      | 5.80E-09           | 5.80E-09              | 2.50E-09                      | 3.65E-09       | 3.37E-08                  | 4.96E-09                    | 3.67E-08                |
| <b>NOx</b>                | <b>kg</b> | 0.00E+00  | 1.93E-02      | 9.29E-03           | 9.29E-03              | 1.86E-03                      | 2.67E-02       | 6.57E-02                  | 1.10E-02                    | 3.71E-03                |
| <b>N<sub>2</sub>O</b>     | <b>kg</b> | 0.00E+00  | 0.00E+00      | 0.00E+00           | 0.00E+00              | 0.00E+00                      | 0.00E+00       | 0.00E+00                  | 0.00E+00                    | 0.00E+00                |
| <b>NMVOC</b>              | <b>kg</b> | 0.00E+00  | 0.00E+00      | 0.00E+00           | 0.00E+00              | 0.00E+00                      | 0.00E+00       | 0.00E+00                  | 0.00E+00                    | 0.00E+00                |
| <b>PM<sub>10</sub></b>    | <b>kg</b> | 0.00E+00  | 0.00E+00      | 0.00E+00           | 0.00E+00              | 0.00E+00                      | 0.00E+00       | 0.00E+00                  | 0.00E+00                    | 0.00E+00                |
| <b>PM<sub>total</sub></b> | <b>kg</b> | 0.00E+00  | 0.00E+00      | 0.00E+00           | 0.00E+00              | 0.00E+00                      | 0.00E+00       | 0.00E+00                  | 0.00E+00                    | 0.00E+00                |
| <b>Se</b>                 | <b>kg</b> | 0.00E+00  | 0.00E+00      | 0.00E+00           | 0.00E+00              | 0.00E+00                      | 0.00E+00       | 0.00E+00                  | 0.00E+00                    | 0.00E+00                |
| <b>SO<sub>2</sub></b>     | <b>kg</b> | 1.20E-02  | 0.00E+00      | 2.88E-02           | 2.88E-02              | 4.60E-03                      | 5.40E-03       | 8.20E-03                  | 2.00E-02                    | 1.36E-02                |
| <b>VOC</b>                | <b>kg</b> | 0.00E+00  | 0.00E+00      | 0.00E+00           | 0.00E+00              | 0.00E+00                      | 0.00E+00       | 0.00E+00                  | 0.00E+00                    | 0.00E+00                |
| <b>Zn</b>                 | <b>kg</b> | 2.90E-07  | 6.30E-07      | 1.13E-05           | 1.13E-05              | 9.10E-08                      | 2.15E-07       | 8.68E-07                  | 9.74E-07                    | 5.43E-07                |

**Table A. 4** – Direct LCI factors of electricity generation. Adapted from [110]

| <b>LCI Factors</b>            | <b>Bituminous coal</b> | <b>Natural gas</b> | <b>Distillate (Diesel) fuel oil</b> | <b>Petroleum coke</b> | <b>Residual (heavy) fuel oil</b> | <b>Nuclear</b> | <b>Hydro</b> | <b>Wood (or other Biomass)</b> | <b>Geothermal</b> | <b>Solar</b> | <b>Wind</b> | <b>Lignite coal</b> |
|-------------------------------|------------------------|--------------------|-------------------------------------|-----------------------|----------------------------------|----------------|--------------|--------------------------------|-------------------|--------------|-------------|---------------------|
| <b>Energy (MJ/kWh)</b>        | 1.08E+01               | 6.70E+00           | 1.04E+01                            | 1.04E+01              | 1.04E+01                         | 0.00E+00       | 0.00E+00     | 0.00E+00                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 1.12E+01            |
| <b>Water (kg/kWh)</b>         | 5.12E+01               | 1.80E+01           | 3.99E+01                            | 0.00E+00              | 3.99E+01                         | 6.02E+01       | 5.81E+01     | 3.10E+00                       | 2.56E+01          | 2.83E+00     | 4.00E-03    | 5.12E+01            |
| <b>Solid waste (kg/kWh)</b>   | 7.21E-02               | 0.00E+00           | 0.00E+00                            | 0.00E+00              | 3.38E-04                         | 0.00E+00       | 2.23E-04     | 4.11E-04                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 1.43E-01            |
| <b>Air Emissions (kg/kWh)</b> |                        |                    |                                     |                       |                                  |                |              |                                |                   |              |             |                     |
| <b>CO<sub>2</sub>-eq</b>      | 9.44E-01               | 4.90E-01           | 7.03E-01                            | 9.70E-01              | 7.83E-01                         | 1.61E-02       | 3.89E-03     | 4.49E-01                       | 9.70E-03          | 2.71E-02     | 7.20E-03    | 1.10E+00            |
| <b>Sb</b>                     | 3.73E-09               | 0.00E+00           | 0.00E+00                            | 0.00E+00              | 0.00E+00                         | 0.00E+00       | 0.00E+00     | 0.00E+00                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 7.04E-09            |
| <b>As</b>                     | 5.55E-08               | 9.56E-10           | 5.26E-08                            | 0.00E+00              | 4.17E-08                         | 0.00E+00       | 0.00E+00     | 0.00E+00                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 1.60E-07            |
| <b>Be</b>                     | 2.22E-09               | 5.73E-11           | 1.11E-09                            | 2.65E-08              | 8.77E-10                         | 0.00E+00       | 0.00E+00     | 0.00E+00                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 8.21E-09            |
| <b>Cd</b>                     | 5.52E-09               | 5.26E-09           | 1.59E-08                            | 1.22E-07              | 1.26E-08                         | 0.00E+00       | 0.00E+00     | 0.00E+00                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 1.99E-08            |
| <b>CO<sub>2</sub></b>         | 9.45E-01               | 4.78E-01           | 8.31E-01                            | 9.70E-01              | 8.02E-01                         | 0.00E+00       | 1.12E-03     | 4.48E-01                       | 2.01E-02          | 0.00E+00     | 0.00E+00    | 1.09E+00            |
| <b>CO</b>                     | 1.30E-04               | 2.14E-04           | 2.16E-04                            | 1.59E-05              | 1.58E-04                         | 0.00E+00       | 4.08E-05     | 3.87E-05                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 9.78E-05            |
| <b>Cr</b>                     | 5.80E-08               | 6.69E-09           | 3.37E-08                            | 2.23E-08              | 2.67E-08                         | 0.00E+00       | 0.00E+00     | 0.00E+00                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 1.33E-07            |
| <b>Co</b>                     | 1.01E-08               | 4.01E-10           | 2.40E-07                            | 0.00E+00              | 1.90E-07                         | 0.00E+00       | 0.00E+00     | 0.00E+00                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 3.91E-08            |
| <b>Cu</b>                     | 2.07E-08               | 5.04E-10           | 0.00E+00                            | 0.00E+00              | 0.00E+00                         | 0.00E+00       | 0.00E+00     | 0.00E+00                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 0.00E+00            |
| <b>CH<sub>2</sub>O</b>        | 5.30E-08               | 4.46E-06           | 1.32E-06                            | 0.00E+00              | 1.04E-06                         | 0.00E+00       | 0.00E+00     | 0.00E+00                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 9.38E-08            |
| <b>Pb</b>                     | 4.31E-08               | 2.39E-09           | 6.02E-08                            | 0.00E+00              | 4.77E-08                         | 0.00E+00       | 6.10E-15     | 0.00E+00                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 1.64E-07            |
| <b>Mn</b>                     | 5.56E-08               | 1.82E-09           | 1.20E-07                            | 0.00E+00              | 9.47E-08                         | 0.00E+00       | 0.00E+00     | 0.00E+00                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 1.92E-07            |
| <b>Hg</b>                     | 2.89E-08               | 1.24E-09           | 4.50E-09                            | 0.00E+00              | 3.57E-09                         | 0.00E+00       | 3.05E-18     | 0.00E+00                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 3.25E-08            |

|                         |          |          |          |          |          |          |          |          |          |          |          |          |
|-------------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| <b>CH<sub>4</sub></b>   | 1.61E-05 | 2.75E-05 | 2.61E-05 | 0.00E+00 | 1.94E-05 | 0.00E+00 | 1.32E-04 | 2.60E-06 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 1.56E-05 |
| <b>Ni</b>               | 5.39E-08 | 1.00E-08 | 3.37E-06 | 3.50E-07 | 2.67E-06 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 1.09E-07 |
| <b>NO<sub>x</sub></b>   | 2.19E-03 | 2.86E-04 | 3.44E-03 | 1.47E-04 | 1.55E-03 | 0.00E+00 | 2.70E-07 | 5.76E-04 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 3.47E-03 |
| <b>N<sub>2</sub>O</b>   | 9.92E-06 | 5.37E-06 | 1.24E-05 | 0.00E+00 | 1.68E-05 | 0.00E+00 | 1.21E-11 | 4.75E-06 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 2.50E-05 |
| <b>NM<sub>VOC</sub></b> | 6.49E-05 | 1.02E-05 | 4.45E-04 | 0.00E+00 | 5.00E-05 | 0.00E+00 | 0.00E+00 | 5.54E-04 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 2.26E-05 |
| <b>PM<sub>10</sub></b>  | 4.17E-05 | 3.61E-05 | 4.30E-05 | 9.45E-08 | 5.99E-05 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| <b>PM total</b>         | 4.77E-03 | 3.31E-05 | 5.53E-04 | 1.86E-05 | 2.51E-03 | 0.00E+00 | 5.32E-06 | 2.64E-05 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 1.11E-03 |
| <b>Se</b>               | 3.41E-07 | 1.15E-10 | 2.72E-08 | 0.00E+00 | 2.16E-08 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 5.08E-07 |
| <b>SO<sub>2</sub></b>   | 4.75E-03 | 2.47E-06 | 1.54E-03 | 5.60E-04 | 9.91E-03 | 0.00E+00 | 1.66E-06 | 2.79E-04 | 7.94E-05 | 0.00E+00 | 0.00E+00 | 4.33E-03 |
| <b>VOC</b>              | 0.00E+00 | 2.64E-05 | 8.64E-06 | 3.53E-06 | 2.39E-05 | 0.00E+00 | 9.87E-08 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| <b>Zn</b>               | 0.00E+00 | 1.72E-08 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |

**Table A. 5** – Upstream LCI factors of electricity generation. Adapted from [110]

| <b>LCI Factors</b>            | <b>Bituminous coal</b> | <b>Natural gas</b> | <b>Distillate (Diesel) fuel oil</b> | <b>Petroleum coke</b> | <b>Residual (heavy) fuel oil</b> | <b>Nuclear</b> | <b>Hydro</b> | <b>Wood (or other Biomass)</b> | <b>Geothermal</b> | <b>Solar</b> | <b>Wind</b> | <b>Lignite coal</b> |
|-------------------------------|------------------------|--------------------|-------------------------------------|-----------------------|----------------------------------|----------------|--------------|--------------------------------|-------------------|--------------|-------------|---------------------|
| <b>Energy (MJ/kWh)</b>        | 3.66E-01               | 3.36E-01           | 7.72E-01                            | 7.72E-01              | 7.72E-01                         | 1.11E+01       | 1.20E-01     | 0.00E+00                       | 2.22E+01          | 1.69E+00     | 2.34E-01    | 5.81E-01            |
| <b>Water (kg/kWh)</b>         | 3.81E+00               | 1.44E+00           | 1.44E+00                            | 0.00E+00              | 1.44E+00                         | 1.19E+02       | 8.00E-02     | 2.97E+02                       | 6.52E+01          | 8.68E-01     | 6.18E-01    | 3.81E+00            |
| <b>Solid waste (kg/kWh)</b>   | 0.00E+00               | 2.61E-04           | 0.00E+00                            | 0.00E+00              | 0.00E+00                         | 0.00E+00       | 8.70E-05     | 4.06E-04                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 0.00E+00            |
| <b>Air Emissions (kg/kWh)</b> |                        |                    |                                     |                       |                                  |                |              |                                |                   |              |             |                     |
| <b>CO<sub>2</sub>-eq</b>      | 4.10E-02               | 1.20E-01           | 1.32E-01                            | 0.00E+00              | 8.91E-02                         | 1.12E-02       | 6.22E-03     | 3.69E-02                       | 6.61E-02          | 9.03E-02     | 2.08E-02    | 0.00E+00            |
| <b>Sb</b>                     | 0.00E+00               | 0.00E+00           | 0.00E+00                            | 0.00E+00              | 0.00E+00                         | 0.00E+00       | 0.00E+00     | 0.00E+00                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 0.00E+00            |
| <b>As</b>                     | 0.00E+00               | 0.00E+00           | 0.00E+00                            | 0.00E+00              | 0.00E+00                         | 0.00E+00       | 0.00E+00     | 0.00E+00                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 0.00E+00            |
| <b>Be</b>                     | 0.00E+00               | 0.00E+00           | 0.00E+00                            | 0.00E+00              | 0.00E+00                         | 0.00E+00       | 0.00E+00     | 0.00E+00                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 0.00E+00            |
| <b>Cd</b>                     | 0.00E+00               | 0.00E+00           | 0.00E+00                            | 0.00E+00              | 0.00E+00                         | 0.00E+00       | 0.00E+00     | 0.00E+00                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 0.00E+00            |
| <b>CO<sub>2</sub></b>         | 2.30E-02               | 6.85E-02           | 7.08E-02                            | 0.00E+00              | 9.90E-02                         | 1.03E-02       | 2.22E-03     | 3.39E-02                       | 4.28E-02          | 1.15E-01     | 1.85E-02    | 0.00E+00            |
| <b>CO</b>                     | 9.60E-05               | 2.60E-04           | 0.00E+00                            | 0.00E+00              | 0.00E+00                         | 0.00E+00       | 7.12E-05     | 7.79E-05                       | 2.08E-04          | 8.54E-05     | 4.84E-05    | 0.00E+00            |
| <b>Cr</b>                     | 0.00E+00               | 0.00E+00           | 0.00E+00                            | 0.00E+00              | 0.00E+00                         | 0.00E+00       | 0.00E+00     | 0.00E+00                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 0.00E+00            |
| <b>Co</b>                     | 0.00E+00               | 0.00E+00           | 0.00E+00                            | 0.00E+00              | 0.00E+00                         | 0.00E+00       | 0.00E+00     | 0.00E+00                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 0.00E+00            |
| <b>Cu</b>                     | 0.00E+00               | 0.00E+00           | 0.00E+00                            | 0.00E+00              | 0.00E+00                         | 0.00E+00       | 0.00E+00     | 0.00E+00                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 0.00E+00            |
| <b>CH<sub>2</sub>O</b>        | 0.00E+00               | 0.00E+00           | 0.00E+00                            | 0.00E+00              | 0.00E+00                         | 0.00E+00       | 0.00E+00     | 0.00E+00                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 0.00E+00            |
| <b>Pb</b>                     | 0.00E+00               | 0.00E+00           | 0.00E+00                            | 0.00E+00              | 0.00E+00                         | 0.00E+00       | 1.04E-14     | 0.00E+00                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 0.00E+00            |
| <b>Mn</b>                     | 0.00E+00               | 0.00E+00           | 0.00E+00                            | 0.00E+00              | 0.00E+00                         | 0.00E+00       | 0.00E+00     | 0.00E+00                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 0.00E+00            |
| <b>Hg</b>                     | 0.00E+00               | 0.00E+00           | 0.00E+00                            | 0.00E+00              | 0.00E+00                         | 0.00E+00       | 5.22E-18     | 0.00E+00                       | 0.00E+00          | 0.00E+00     | 0.00E+00    | 0.00E+00            |
| <b>CH<sub>4</sub></b>         | 1.16E-03               | 2.76E-03           | 1.96E-03                            | 0.00E+00              | 2.24E-03                         | 2.00E-05       | 5.00E-06     | 4.72E-06                       | 6.08E-05          | 4.59E-04     | 6.32E-05    | 0.00E+00            |

|                       |          |          |          |          |          |          |          |          |          |          |          |          |
|-----------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| <b>Ni</b>             | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| <b>NOx</b>            | 2.27E-04 | 4.75E-04 | 5.19E-04 | 0.00E+00 | 3.20E-04 | 5.36E-05 | 6.36E-06 | 1.93E-04 | 1.04E-04 | 4.16E-04 | 3.81E-05 | 0.00E+00 |
| <b>N<sub>2</sub>O</b> | 1.06E-06 | 7.19E-07 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 5.00E-07 | 5.03E-08 | 9.36E-06 | 1.35E-06 | 2.00E-07 | 3.00E-07 | 0.00E+00 |
| <b>NMVOC</b>          | 1.19E-04 | 6.18E-04 | 1.24E-03 | 0.00E+00 | 1.41E-03 | 9.00E-06 | 0.00E+00 | 7.32E-05 | 4.00E-06 | 2.85E-05 | 8.57E-06 | 0.00E+00 |
| <b>PM10</b>           | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| <b>PM total</b>       | 2.53E-03 | 7.13E-05 | 9.20E-05 | 0.00E+00 | 9.00E-05 | 1.74E-05 | 1.98E-05 | 2.69E-05 | 3.27E-05 | 6.05E-05 | 2.63E-05 | 0.00E+00 |
| <b>Se</b>             | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| <b>SO<sub>2</sub></b> | 1.79E-04 | 3.22E-04 | 7.17E-04 | 0.00E+00 | 4.30E-04 | 4.92E-05 | 6.05E-06 | 3.90E-05 | 1.31E-03 | 2.32E-04 | 4.67E-05 | 0.00E+00 |
| <b>VOC</b>            | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 2.75E-07 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |
| <b>Zn</b>             | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 | 0.00E+00 |

Table A. 6 - Total LCI data for U.S. electricity generation by state.

| Abbreviation | Energy   | Water    | Solid waste | Sb       | As       | Be       | Cd       | CO <sub>2</sub> | CO       | Cr       | Co       | Cu       | CH <sub>2</sub> O | Pb       | Mn       | Hg       | CH <sub>4</sub> | Ni       | NOx      | N <sub>2</sub> O | NM VOC   | PM10     | PMtotal  | Se       | SO <sub>2</sub> | VOC<br>(unspecified) | Zn       |          |
|--------------|----------|----------|-------------|----------|----------|----------|----------|-----------------|----------|----------|----------|----------|-------------------|----------|----------|----------|-----------------|----------|----------|------------------|----------|----------|----------|----------|-----------------|----------------------|----------|----------|
|              | (MJ/kWh) | (kg/kWh) | (kg/kWh)    | (kg/kWh) | (kg/kWh) | (kg/kWh) | (kg/kWh) | (kg/kWh)        | (kg/kWh) | (kg/kWh) | (kg/kWh) | (kg/kWh) | (kg/kWh)          | (kg/kWh) | (kg/kWh) | (kg/kWh) | (kg/kWh)        | (kg/kWh) | (kg/kWh) | (kg/kWh)         | (kg/kWh) | (kg/kWh) | (kg/kWh) | (kg/kWh) | (kg/kWh)        | (kg/kWh)             | (kg/kWh) | (kg/kWh) |
| AK           | 9.97E+00 | 3.72E+01 | 6.97E-03    | 3.50E-10 | 1.26E-08 | 3.81E-10 | 5.13E-09 | 4.66E-01        | 3.08E-04 | 1.31E-08 | 3.26E-08 | 2.18E-09 | 2.32E-06          | 1.31E-08 | 2.18E-08 | 3.89E-09 | 1.72E-03        | 4.52E-07 | 6.28E-03 | 4.61E-06         | 5.44E-04 | 2.69E-05 | 8.27E-04 | 3.56E-08 | 5.19E-04        | 1.39E-05             | 8.25E-09 |          |
| AL           | 1.27E+01 | 8.13E+01 | 1.75E-02    | 8.98E-10 | 1.38E-08 | 5.58E-10 | 3.47E-09 | 4.51E-01        | 2.55E-04 | 1.67E-08 | 2.67E-09 | 5.19E-09 | 1.82E-06          | 1.14E-08 | 1.42E-08 | 7.46E-09 | 1.44E-03        | 1.81E-08 | 6.34E-04 | 5.44E-06         | 3.17E-04 | 2.47E-05 | 1.81E-03 | 8.21E-08 | 3.72E-04        | 1.07E-05             | 6.98E-09 |          |
| AR           | 1.25E+01 | 7.76E+01 | 2.85E-02    | 1.47E-09 | 2.22E-08 | 8.93E-10 | 3.77E-09 | 5.39E-01        | 2.41E-04 | 2.49E-08 | 4.27E-09 | 8.31E-09 | 1.36E-06          | 1.77E-08 | 2.25E-08 | 1.18E-08 | 1.34E-03        | 2.66E-08 | 1.10E-03 | 7.76E-06         | 2.79E-04 | 2.73E-05 | 2.91E-03 | 1.34E-07 | 9.11E-04        | 7.97E-06             | 5.17E-09 |          |
| AZ           | 1.36E+01 | 7.95E+01 | 2.03E-02    | 1.04E-09 | 1.58E-08 | 6.39E-10 | 3.21E-09 | 4.58E-01        | 2.23E-04 | 1.83E-08 | 3.06E-09 | 5.95E-09 | 1.42E-06          | 1.28E-08 | 1.62E-08 | 8.48E-09 | 1.25E-03        | 1.98E-08 | 8.01E-04 | 5.69E-06         | 2.55E-04 | 2.30E-05 | 2.08E-03 | 9.54E-08 | 2.83E-04        | 8.33E-06             | 5.41E-09 |          |
| CA           | 1.15E+01 | 5.07E+01 | 3.19E-04    | 6.10E-12 | 6.14E-10 | 3.31E-11 | 2.64E-09 | 2.57E-01        | 2.80E-04 | 3.45E-09 | 4.32E-10 | 2.85E-10 | 2.22E-06          | 1.31E-09 | 1.10E-09 | 6.68E-10 | 1.44E-03        | 8.10E-09 | 7.16E-04 | 2.18E-06         | 3.38E-04 | 1.81E-05 | 8.11E-05 | 6.39E-10 | 2.87E-04        | 1.32E-05             | 8.56E-09 |          |

OLI

| IA       | HI       | GA       | FL       | DE       | DC       | CT       | CO       |
|----------|----------|----------|----------|----------|----------|----------|----------|
| 1.13E+01 | 1.17E+01 | 1.25E+01 | 1.07E+01 | 8.31E+00 | 3.22E+01 | 1.47E+01 | 1.06E+01 |
| 4.49E+01 | 4.19E+01 | 8.10E+01 | 5.08E+01 | 2.15E+01 | 1.86E+01 | 1.00E+02 | 3.77E+01 |
| 3.34E-02 | 1.19E-02 | 2.05E-02 | 1.23E-02 | 4.36E-03 | 2.50E-04 | 5.08E-04 | 3.96E-02 |
| 1.73E-09 | 6.06E-10 | 1.05E-09 | 6.26E-10 | 2.13E-10 | 0.00E+00 | 1.84E-11 | 2.04E-09 |
| 2.60E-08 | 4.05E-08 | 1.61E-08 | 1.01E-08 | 4.44E-09 | 9.16E-10 | 8.71E-10 | 3.06E-08 |
| 1.04E-09 | 1.02E-09 | 6.51E-10 | 6.41E-10 | 1.88E-10 | 5.49E-11 | 4.21E-11 | 1.23E-09 |
| 2.93E-09 | 1.04E-08 | 3.65E-09 | 5.56E-09 | 5.31E-09 | 5.04E-09 | 2.69E-09 | 4.25E-09 |
| 4.75E-01 | 7.65E-01 | 4.93E-01 | 5.17E-01 | 4.69E-01 | 2.84E-01 | 2.66E-01 | 6.99E-01 |
| 1.52E-04 | 1.69E-04 | 2.58E-04 | 3.61E-04 | 4.55E-04 | 4.54E-04 | 2.42E-04 | 2.47E-04 |
| 2.74E-08 | 2.96E-08 | 1.91E-08 | 1.45E-08 | 9.77E-09 | 6.41E-09 | 3.71E-09 | 3.33E-08 |
| 5.93E-09 | 1.45E-07 | 3.39E-09 | 2.69E-09 | 2.68E-09 | 3.84E-10 | 7.92E-10 | 5.66E-09 |
| 9.62E-09 | 3.36E-09 | 6.04E-09 | 3.81E-09 | 1.65E-09 | 4.83E-10 | 3.54E-10 | 1.15E-08 |
| 2.74E-07 | 7.94E-07 | 1.77E-06 | 3.02E-06 | 4.15E-06 | 4.27E-06 | 2.23E-06 | 1.06E-06 |
| 2.04E-08 | 4.30E-08 | 1.32E-08 | 9.02E-09 | 5.12E-09 | 2.29E-09 | 1.54E-09 | 2.42E-08 |
| 2.65E-08 | 8.06E-08 | 1.66E-08 | 1.09E-08 | 5.73E-09 | 1.74E-09 | 1.45E-09 | 3.09E-08 |
| 1.35E-08 | 7.39E-09 | 8.65E-09 | 5.70E-09 | 2.84E-09 | 1.19E-09 | 7.73E-10 | 1.61E-08 |
| 7.46E-04 | 1.85E-03 | 1.46E-03 | 2.10E-03 | 2.66E-03 | 2.65E-03 | 1.43E-03 | 1.36E-03 |
| 4.27E-08 | 2.02E-06 | 2.45E-08 | 2.90E-08 | 3.66E-08 | 9.58E-09 | 1.29E-08 | 3.23E-08 |
| 9.13E-04 | 4.26E-03 | 6.29E-04 | 8.72E-04 | 8.19E-04 | 4.60E-03 | 5.72E-04 | 1.27E-03 |
| 7.99E-06 | 1.11E-05 | 6.93E-06 | 5.45E-06 | 2.54E-06 | 1.60E-06 | 4.45E-06 | 1.04E-05 |
| 1.35E-04 | 1.11E-03 | 3.26E-04 | 4.73E-04 | 6.06E-04 | 6.02E-04 | 3.38E-04 | 2.50E-04 |
| 2.15E-05 | 4.77E-05 | 2.60E-05 | 3.15E-05 | 3.62E-05 | 3.46E-05 | 1.84E-05 | 3.12E-05 |
| 3.40E-03 | 2.81E-03 | 2.11E-03 | 1.30E-03 | 5.22E-04 | 1.00E-04 | 1.02E-04 | 4.03E-03 |
| 1.58E-07 | 7.17E-08 | 9.63E-08 | 5.73E-08 | 1.98E-08 | 1.10E-10 | 1.80E-09 | 1.87E-07 |
| 6.01E-04 | 3.82E-03 | 3.57E-04 | 4.26E-04 | 3.71E-04 | 3.53E-04 | 2.03E-04 | 5.03E-04 |
| 1.49E-06 | 1.52E-05 | 1.04E-05 | 1.79E-05 | 2.46E-05 | 2.53E-05 | 1.32E-05 | 6.14E-06 |
| 9.37E-10 | 0.00E+00 | 6.77E-09 | 1.16E-08 | 1.60E-08 | 1.65E-08 | 8.60E-09 | 3.99E-09 |

LI

| MD       | MA       | LA       | KY       | KS       | NZ       | IL       | ID       |
|----------|----------|----------|----------|----------|----------|----------|----------|
| 1.57E+01 | 1.14E+01 | 9.38E+00 | 1.13E+01 | 1.30E+01 | 1.12E+01 | 1.68E+01 | 9.36E+00 |
| 1.02E+02 | 6.04E+01 | 5.70E+01 | 5.21E+01 | 5.89E+01 | 4.58E+01 | 1.15E+02 | 4.87E+01 |
| 2.71E-02 | 4.50E-03 | 8.49E-03 | 6.01E-02 | 3.50E-02 | 5.28E-02 | 2.29E-02 | 3.98E-04 |
| 1.40E-09 | 2.21E-10 | 4.29E-10 | 3.11E-09 | 1.81E-09 | 2.73E-09 | 1.18E-09 | 6.98E-12 |
| 2.12E-08 | 4.51E-09 | 7.00E-09 | 4.64E-08 | 2.70E-08 | 4.09E-08 | 1.77E-08 | 3.07E-10 |
| 8.46E-10 | 1.82E-10 | 1.51E-09 | 2.22E-09 | 1.08E-09 | 1.77E-09 | 7.11E-10 | 1.64E-11 |
| 2.91E-09 | 4.02E-09 | 9.60E-09 | 6.84E-09 | 2.92E-09 | 5.72E-09 | 2.25E-09 | 1.13E-09 |
| 4.84E-01 | 4.26E-01 | 4.48E-01 | 9.13E-01 | 5.64E-01 | 8.54E-01 | 3.88E-01 | 1.06E-01 |
| 1.63E-04 | 3.42E-04 | 3.33E-04 | 2.43E-04 | 1.45E-04 | 2.65E-04 | 1.19E-04 | 1.79E-04 |
| 2.29E-08 | 8.29E-09 | 1.20E-08 | 4.93E-08 | 2.85E-08 | 4.39E-08 | 1.91E-08 | 1.53E-09 |
| 4.85E-09 | 3.48E-09 | 1.46E-09 | 8.77E-09 | 5.07E-09 | 7.76E-09 | 3.33E-09 | 1.04E-10 |
| 7.84E-09 | 1.57E-09 | 2.70E-09 | 1.73E-08 | 1.01E-08 | 1.52E-08 | 6.62E-09 | 1.46E-10 |
| 6.82E-07 | 3.00E-06 | 2.85E-06 | 5.03E-07 | 2.17E-07 | 9.40E-07 | 4.35E-07 | 9.50E-07 |
| 1.68E-08 | 4.81E-09 | 6.49E-09 | 3.62E-08 | 2.11E-08 | 3.21E-08 | 1.39E-08 | 5.90E-10 |
| 2.16E-08 | 5.82E-09 | 7.58E-09 | 4.67E-08 | 2.72E-08 | 4.12E-08 | 1.79E-08 | 4.92E-10 |
| 1.10E-08 | 2.59E-09 | 4.11E-09 | 2.42E-08 | 1.41E-08 | 2.14E-08 | 9.30E-09 | 3.18E-10 |
| 8.97E-04 | 2.00E-03 | 1.92E-03 | 1.34E-03 | 7.63E-04 | 1.50E-03 | 6.64E-04 | 6.08E-04 |
| 3.58E-08 | 4.66E-08 | 2.93E-08 | 5.52E-08 | 2.86E-08 | 4.73E-08 | 1.93E-08 | 2.23E-09 |
| 7.72E-04 | 8.02E-04 | 1.12E-03 | 1.56E-03 | 8.99E-04 | 1.80E-03 | 4.89E-04 | 3.56E-04 |
| 8.56E-06 | 6.89E-06 | 4.10E-06 | 1.55E-05 | 9.34E-06 | 1.32E-05 | 6.15E-06 | 1.01E-06 |
| 1.82E-04 | 4.77E-04 | 4.40E-04 | 2.23E-04 | 1.21E-04 | 2.67E-04 | 1.25E-04 | 1.57E-04 |
| 2.12E-05 | 2.74E-05 | 2.78E-05 | 3.85E-05 | 2.18E-05 | 3.78E-05 | 1.66E-05 | 7.77E-06 |
| 2.77E-03 | 5.42E-04 | 9.12E-04 | 6.09E-03 | 3.56E-03 | 5.37E-03 | 2.34E-03 | 5.69E-05 |
| 1.28E-07 | 2.06E-08 | 3.93E-08 | 2.84E-07 | 1.66E-07 | 2.50E-07 | 1.08E-07 | 6.63E-10 |
| 5.68E-04 | 3.50E-04 | 5.63E-04 | 1.05E-03 | 2.60E-04 | 9.86E-04 | 5.49E-04 | 1.18E-04 |
| 3.95E-06 | 1.80E-05 | 1.70E-05 | 2.78E-06 | 1.13E-06 | 5.36E-06 | 2.47E-06 | 5.84E-06 |
| 2.53E-09 | 1.15E-08 | 1.09E-08 | 1.76E-09 | 7.33E-10 | 3.47E-09 | 1.61E-09 | 3.66E-09 |



| ND       | NC       | MT       | MS       | MO       | MN       | MI       | ME       |
|----------|----------|----------|----------|----------|----------|----------|----------|
| 1.16E+01 | 1.37E+01 | 1.12E+01 | 9.77E+00 | 1.24E+01 | 1.32E+01 | 1.39E+01 | 9.10E+00 |
| 4.24E+01 | 8.87E+01 | 5.04E+01 | 4.43E+01 | 6.69E+01 | 7.75E+01 | 8.38E+01 | 9.78E+01 |
| 5.08E-02 | 2.08E-02 | 3.76E-02 | 6.35E-03 | 5.55E-02 | 2.84E-02 | 2.64E-02 | 8.25E-04 |
| 2.63E-09 | 1.07E-09 | 1.94E-09 | 3.17E-10 | 2.87E-09 | 1.47E-09 | 1.36E-09 | 2.34E-11 |
| 3.91E-08 | 1.64E-08 | 2.89E-08 | 5.49E-09 | 4.28E-08 | 2.20E-08 | 2.06E-08 | 1.03E-09 |
| 1.57E-09 | 6.58E-10 | 1.59E-09 | 2.35E-10 | 1.71E-09 | 8.81E-10 | 9.94E-10 | 4.00E-11 |
| 4.05E-09 | 3.21E-09 | 4.99E-09 | 4.66E-09 | 4.67E-09 | 2.97E-09 | 4.19E-09 | 1.80E-09 |
| 7.77E-01 | 4.28E-01 | 5.83E-01 | 4.85E-01 | 7.90E-01 | 4.85E-01 | 5.30E-01 | 1.87E-01 |
| 1.89E-04 | 2.17E-04 | 1.71E-04 | 4.00E-04 | 2.13E-04 | 1.75E-04 | 2.14E-04 | 2.18E-04 |
| 4.10E-08 | 1.88E-08 | 3.07E-08 | 1.03E-08 | 4.52E-08 | 2.38E-08 | 2.31E-08 | 2.71E-09 |
| 7.31E-09 | 3.49E-09 | 5.31E-09 | 1.25E-09 | 8.04E-09 | 4.16E-09 | 4.05E-09 | 1.94E-09 |
| 1.46E-08 | 6.11E-09 | 1.08E-08 | 2.16E-09 | 1.60E-08 | 8.21E-09 | 7.69E-09 | 2.88E-10 |
| 1.65E-07 | 1.36E-06 | 1.05E-07 | 3.56E-06 | 3.85E-07 | 6.96E-07 | 1.20E-06 | 1.41E-06 |
| 3.05E-08 | 1.32E-08 | 2.25E-08 | 5.58E-09 | 3.34E-08 | 1.73E-08 | 1.64E-08 | 1.46E-09 |
| 3.93E-08 | 1.68E-08 | 2.90E-08 | 6.21E-09 | 4.30E-08 | 2.22E-08 | 2.09E-08 | 1.79E-09 |
| 2.04E-08 | 8.70E-09 | 1.51E-08 | 3.44E-09 | 2.23E-08 | 1.15E-08 | 1.09E-08 | 6.04E-10 |
| 9.69E-04 | 1.23E-03 | 7.20E-04 | 2.31E-03 | 1.17E-03 | 9.45E-04 | 1.19E-03 | 9.82E-04 |
| 4.09E-08 | 2.50E-08 | 3.47E-08 | 1.35E-08 | 4.56E-08 | 2.45E-08 | 2.81E-08 | 2.81E-08 |
| 1.94E-03 | 7.54E-04 | 1.16E-03 | 8.26E-04 | 1.53E-03 | 7.90E-04 | 9.81E-04 | 7.28E-04 |
| 1.31E-05 | 5.87E-06 | 9.68E-06 | 3.66E-06 | 1.37E-05 | 9.16E-06 | 8.20E-06 | 1.31E-05 |
| 1.50E-04 | 2.62E-04 | 1.08E-04 | 5.33E-04 | 1.94E-04 | 1.92E-04 | 2.52E-04 | 3.70E-04 |
| 3.04E-05 | 2.30E-05 | 2.23E-05 | 3.23E-05 | 3.49E-05 | 2.19E-05 | 2.48E-05 | 1.22E-05 |
| 5.15E-03 | 2.14E-03 | 3.81E-03 | 7.07E-04 | 5.63E-03 | 2.89E-03 | 2.70E-03 | 1.27E-04 |
| 2.40E-07 | 9.82E-08 | 1.77E-07 | 2.91E-08 | 2.62E-07 | 1.34E-07 | 1.25E-07 | 2.37E-09 |
| 1.23E-03 | 3.75E-04 | 5.68E-04 | 3.51E-04 | 1.32E-03 | 4.04E-04 | 8.66E-04 | 2.56E-04 |
| 7.75E-07 | 7.99E-06 | 6.56E-07 | 2.10E-05 | 2.05E-06 | 4.00E-06 | 7.01E-06 | 8.62E-06 |
| 4.88E-10 | 5.19E-09 | 2.99E-10 | 1.37E-08 | 1.32E-09 | 2.60E-09 | 4.54E-09 | 5.40E-09 |

| OK       | OH       | NY       | NV       | NM       | NJ       | NH       | NE       |
|----------|----------|----------|----------|----------|----------|----------|----------|
| 9.84E+00 | 1.21E+01 | 1.35E+01 | 1.08E+01 | 1.07E+01 | 1.40E+01 | 1.68E+01 | 1.37E+01 |
| 2.59E+01 | 6.44E+01 | 8.15E+01 | 2.78E+01 | 3.71E+01 | 8.27E+01 | 1.36E+02 | 8.14E+01 |
| 1.77E-02 | 4.20E-02 | 1.14E-03 | 4.14E-03 | 4.03E-02 | 1.40E-03 | 1.74E-03 | 4.32E-02 |
| 9.08E-10 | 2.17E-09 | 4.93E-11 | 2.04E-10 | 2.08E-09 | 6.45E-11 | 8.18E-11 | 2.24E-09 |
| 1.40E-08 | 3.26E-08 | 1.36E-09 | 3.74E-09 | 3.14E-08 | 1.61E-09 | 1.55E-09 | 3.33E-08 |
| 5.67E-10 | 1.53E-09 | 5.82E-11 | 1.63E-10 | 1.26E-09 | 7.35E-11 | 6.48E-11 | 1.33E-09 |
| 3.79E-09 | 5.54E-09 | 2.37E-09 | 4.14E-09 | 4.70E-09 | 3.16E-09 | 1.45E-09 | 3.39E-09 |
| 5.16E-01 | 6.97E-01 | 2.45E-01 | 4.13E-01 | 7.52E-01 | 2.98E-01 | 1.68E-01 | 6.01E-01 |
| 2.92E-04 | 2.50E-04 | 2.31E-04 | 3.87E-04 | 2.78E-04 | 2.78E-04 | 1.40E-04 | 1.50E-04 |
| 1.72E-08 | 3.56E-08 | 3.74E-09 | 8.05E-09 | 3.45E-08 | 4.92E-09 | 2.98E-09 | 3.49E-08 |
| 2.70E-09 | 6.36E-09 | 1.30E-09 | 9.10E-10 | 6.14E-09 | 8.67E-10 | 7.37E-10 | 6.06E-09 |
| 5.27E-09 | 1.22E-08 | 4.87E-10 | 1.50E-09 | 1.17E-08 | 6.48E-10 | 5.79E-10 | 1.24E-08 |
| 2.08E-06 | 1.12E-06 | 1.90E-06 | 3.25E-06 | 1.38E-06 | 2.57E-06 | 1.10E-06 | 9.75E-08 |
| 1.16E-08 | 2.58E-08 | 1.83E-09 | 4.11E-09 | 2.49E-08 | 2.24E-09 | 1.64E-09 | 2.59E-08 |
| 1.44E-08 | 3.30E-08 | 2.00E-09 | 4.39E-09 | 3.18E-08 | 2.24E-09 | 1.88E-09 | 3.34E-08 |
| 7.61E-09 | 1.71E-08 | 9.26E-10 | 2.48E-09 | 1.65E-08 | 1.22E-09 | 9.48E-10 | 1.73E-08 |
| 1.61E-03 | 1.41E-03 | 1.22E-03 | 2.13E-03 | 1.57E-03 | 1.64E-03 | 7.70E-04 | 8.11E-04 |
| 1.85E-08 | 4.22E-08 | 1.89E-08 | 1.12E-08 | 3.84E-08 | 1.32E-08 | 9.51E-09 | 3.25E-08 |
| 9.41E-04 | 1.17E-03 | 5.57E-04 | 8.55E-04 | 2.42E-03 | 5.32E-04 | 3.81E-04 | 1.18E-03 |
| 5.70E-06 | 1.09E-05 | 2.46E-06 | 2.08E-06 | 1.08E-05 | 2.45E-06 | 7.21E-06 | 1.04E-05 |
| 3.42E-04 | 2.69E-04 | 2.90E-04 | 4.71E-04 | 2.97E-04 | 3.72E-04 | 2.22E-04 | 1.24E-04 |
| 2.69E-05 | 3.32E-05 | 1.61E-05 | 2.86E-05 | 3.43E-05 | 2.16E-05 | 9.93E-06 | 2.55E-05 |
| 1.83E-03 | 4.28E-03 | 1.62E-04 | 4.83E-04 | 4.11E-03 | 1.95E-04 | 2.06E-04 | 4.39E-03 |
| 8.31E-08 | 1.98E-07 | 4.67E-09 | 1.87E-08 | 1.90E-07 | 6.02E-09 | 7.56E-09 | 2.04E-07 |
| 7.84E-04 | 1.00E-03 | 2.22E-04 | 4.46E-04 | 4.37E-04 | 2.36E-04 | 1.53E-04 | 1.39E-03 |
| 1.23E-05 | 6.51E-06 | 1.14E-05 | 1.92E-05 | 8.01E-06 | 1.52E-05 | 6.57E-06 | 3.98E-07 |
| 7.98E-09 | 4.21E-09 | 7.29E-09 | 1.25E-08 | 5.21E-09 | 9.91E-09 | 4.24E-09 | 2.53E-10 |

| UT       | TX       | TN       | SD       | SC       | RI       | PA       | OR       |
|----------|----------|----------|----------|----------|----------|----------|----------|
| 1.03E+01 | 1.04E+01 | 1.48E+01 | 1.03E+01 | 1.69E+01 | 8.42E+00 | 1.46E+01 | 9.48E+00 |
| 4.47E+01 | 4.27E+01 | 9.89E+01 | 3.60E+01 | 1.26E+02 | 1.94E+01 | 9.36E+01 | 4.55E+01 |
| 4.96E-02 | 1.95E-02 | 2.82E-02 | 1.32E-02 | 1.55E-02 | 2.58E-04 | 1.85E-02 | 2.53E-03 |
| 2.56E-09 | 1.00E-09 | 1.45E-09 | 6.74E-10 | 8.00E-10 | 0.00E+00 | 9.51E-10 | 1.18E-10 |
| 3.84E-08 | 1.54E-08 | 2.18E-08 | 1.01E-08 | 1.21E-08 | 1.16E-09 | 1.46E-08 | 2.00E-09 |
| 1.54E-09 | 6.26E-10 | 8.75E-10 | 4.06E-10 | 4.87E-10 | 6.13E-11 | 5.86E-10 | 8.47E-11 |
| 5.01E-09 | 4.13E-09 | 2.92E-09 | 1.42E-09 | 2.08E-09 | 5.27E-09 | 3.11E-09 | 1.51E-09 |
| 7.74E-01 | 5.20E-01 | 4.73E-01 | 2.49E-01 | 3.09E-01 | 4.63E-01 | 4.20E-01 | 1.61E-01 |
| 2.73E-04 | 3.06E-04 | 1.66E-04 | 1.41E-04 | 1.33E-04 | 4.70E-04 | 2.12E-04 | 2.01E-04 |
| 4.14E-08 | 1.90E-08 | 2.36E-08 | 1.10E-08 | 1.36E-08 | 6.76E-09 | 1.70E-08 | 3.53E-09 |
| 7.23E-09 | 3.02E-09 | 4.36E-09 | 1.92E-09 | 2.51E-09 | 1.39E-09 | 3.11E-09 | 4.21E-10 |
| 1.43E-08 | 5.82E-09 | 8.13E-09 | 3.78E-09 | 4.52E-09 | 4.98E-10 | 5.44E-09 | 7.82E-10 |
| 1.06E-06 | 2.25E-06 | 6.54E-07 | 3.65E-07 | 7.58E-07 | 4.42E-06 | 1.43E-06 | 1.14E-06 |
| 3.02E-08 | 1.28E-08 | 1.72E-08 | 7.99E-09 | 9.71E-09 | 2.61E-09 | 1.19E-08 | 1.97E-09 |
| 3.87E-08 | 1.59E-08 | 2.21E-08 | 1.02E-08 | 1.24E-08 | 2.30E-09 | 1.50E-08 | 2.22E-09 |
| 2.01E-08 | 8.40E-09 | 1.14E-08 | 5.32E-09 | 6.41E-09 | 1.25E-09 | 7.77E-09 | 1.23E-09 |
| 1.52E-03 | 1.74E-03 | 8.87E-04 | 4.75E-04 | 7.35E-04 | 2.75E-03 | 1.21E-03 | 7.59E-04 |
| 4.21E-08 | 2.10E-08 | 2.75E-08 | 1.14E-08 | 1.72E-08 | 2.38E-08 | 2.26E-08 | 4.25E-09 |
| 1.85E-03 | 8.72E-04 | 6.67E-04 | 2.94E-04 | 4.33E-04 | 6.72E-04 | 9.51E-04 | 5.03E-04 |
| 1.18E-05 | 5.76E-06 | 7.62E-06 | 3.54E-06 | 4.94E-06 | 1.62E-06 | 5.79E-06 | 1.80E-06 |
| 2.73E-04 | 3.69E-04 | 1.74E-04 | 8.65E-05 | 1.67E-04 | 6.28E-04 | 2.60E-04 | 1.77E-04 |
| 3.70E-05 | 2.93E-05 | 2.14E-05 | 1.04E-05 | 1.50E-05 | 3.59E-05 | 2.22E-05 | 1.05E-05 |
| 5.04E-03 | 2.02E-03 | 2.87E-03 | 1.35E-03 | 1.60E-03 | 1.06E-04 | 1.90E-03 | 2.76E-04 |
| 2.34E-07 | 9.18E-08 | 1.33E-07 | 6.16E-08 | 7.32E-08 | 2.26E-10 | 8.71E-08 | 1.08E-08 |
| 6.20E-04 | 7.15E-04 | 5.00E-04 | 1.40E-04 | 2.31E-04 | 3.33E-04 | 6.04E-04 | 1.64E-04 |
| 6.09E-06 | 1.32E-05 | 3.78E-06 | 2.26E-06 | 4.43E-06 | 2.61E-05 | 8.40E-06 | 6.93E-06 |
| 3.96E-09 | 8.62E-09 | 2.43E-09 | 1.37E-09 | 2.87E-09 | 1.70E-08 | 5.46E-09 | 4.38E-09 |

| U.S.     | WY       | WV       | WI       | WA       | VT       | VA       |
|----------|----------|----------|----------|----------|----------|----------|
| 1.23E+01 | 1.12E+01 | 1.09E+01 | 1.21E+01 | 1.08E+01 | 1.10E+01 | 1.34E+01 |
| 6.80E+01 | 4.93E+01 | 5.35E+01 | 7.03E+01 | 6.48E+01 | 1.08E+02 | 8.97E+01 |
| 2.21E-02 | 6.24E-02 | 6.79E-02 | 3.71E-02 | 3.17E-03 | 3.79E-04 | 1.29E-02 |
| 1.14E-09 | 3.23E-09 | 3.51E-09 | 1.92E-09 | 1.51E-10 | 0.00E+00 | 6.60E-10 |
| 1.74E-08 | 4.81E-08 | 5.24E-08 | 2.88E-08 | 2.35E-09 | 9.83E-13 | 1.05E-08 |
| 7.77E-10 | 1.92E-09 | 2.09E-09 | 1.20E-09 | 9.57E-11 | 5.89E-14 | 4.24E-10 |
| 3.87E-09 | 4.89E-09 | 5.31E-09 | 4.31E-09 | 7.35E-10 | 5.41E-12 | 3.37E-09 |
| 4.85E-01 | 9.42E-01 | 9.19E-01 | 6.61E-01 | 9.66E-02 | 4.20E-02 | 4.09E-01 |
| 2.44E-04 | 2.11E-04 | 2.24E-04 | 2.38E-04 | 1.38E-04 | 1.03E-04 | 2.56E-04 |
| 2.01E-08 | 5.04E-08 | 5.48E-08 | 3.15E-08 | 3.00E-09 | 6.88E-12 | 1.34E-08 |
| 3.87E-09 | 9.04E-09 | 9.91E-09 | 5.42E-09 | 4.94E-10 | 4.12E-13 | 3.22E-09 |
| 6.49E-09 | 1.79E-08 | 1.95E-08 | 1.08E-08 | 8.87E-10 | 5.18E-13 | 3.88E-09 |
| 1.54E-06 | 1.24E-07 | 1.24E-07 | 1.09E-06 | 4.33E-07 | 4.59E-09 | 1.97E-06 |
| 1.41E-08 | 3.74E-08 | 4.07E-08 | 2.28E-08 | 1.99E-09 | 2.47E-12 | 8.99E-09 |
| 1.79E-08 | 4.83E-08 | 5.26E-08 | 2.91E-08 | 2.45E-09 | 1.87E-12 | 1.13E-08 |
| 9.26E-09 | 2.50E-08 | 2.72E-08 | 1.52E-08 | 1.29E-09 | 1.27E-12 | 5.68E-09 |
| 1.35E-03 | 1.16E-03 | 1.24E-03 | 1.29E-03 | 3.28E-04 | 1.04E-04 | 1.47E-03 |
| 3.00E-08 | 5.09E-08 | 5.64E-08 | 3.26E-08 | 3.80E-09 | 1.03E-11 | 3.16E-08 |
| 1.17E-03 | 1.66E-03 | 1.41E-03 | 8.62E-04 | 2.16E-04 | 4.47E-04 | 7.79E-04 |
| 7.30E-06 | 1.55E-05 | 1.60E-05 | 1.01E-05 | 1.74E-06 | 1.19E-05 | 6.52E-06 |
| 2.87E-04 | 1.73E-04 | 1.86E-04 | 2.61E-04 | 8.09E-05 | 1.60E-04 | 3.48E-04 |
| 2.52E-05 | 3.68E-05 | 3.99E-05 | 3.01E-05 | 5.19E-06 | 3.71E-08 | 2.35E-05 |
| 2.28E-03 | 6.33E-03 | 6.88E-03 | 3.78E-03 | 3.27E-04 | 3.35E-05 | 1.35E-03 |
| 1.04E-07 | 2.95E-07 | 3.21E-07 | 1.75E-07 | 1.38E-08 | 1.18E-13 | 6.05E-08 |
| 5.72E-04 | 7.98E-04 | 7.12E-04 | 4.08E-04 | 7.35E-05 | 3.37E-05 | 3.10E-04 |
| 9.06E-06 | 4.68E-07 | 4.48E-07 | 6.32E-06 | 2.81E-06 | 2.38E-07 | 1.17E-05 |
| 5.84E-09 | 2.93E-10 | 2.77E-10 | 4.10E-09 | 1.66E-09 | 1.77E-11 | 7.54E-09 |

## Appendix C: Case Studies – Supplementary Data

Table A. 7 – Cement plants in California in 2016 [147]

| Company       | Plant Location |
|---------------|----------------|
| CalPortland   | Mojave         |
| CalPortland   | Oro Grande     |
| CEMEX         | Victorville    |
| Lehigh Hanson | Cupertino      |
| Lehigh Hanson | Redding        |
| Lehigh Hanson | Tehachapi      |
| Mitsubishi    | Lucerne Valley |
| National      | Lebec          |

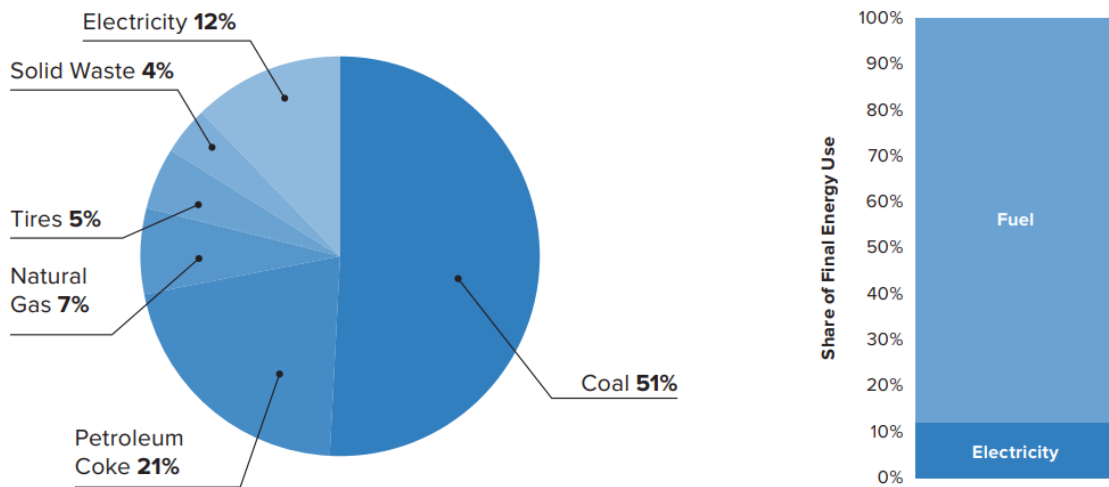


Figure A. 3 – 2015 energy mix in the cement industry in California. Figure adopted from [147]

**Table A. 8** – 2015 California’s average kiln fuel mix in cement plants. Data calculated based on [147]

| <b>2015 California Kiln Fuel Mix</b> |             |
|--------------------------------------|-------------|
| Coal                                 | 58%         |
| Petcoke                              | 24%         |
| Natural gas                          | 8%          |
| Waste tires                          | 6%          |
| Solid waste                          | 4%          |
| <b>Total</b>                         | <b>100%</b> |