

This is a repository copy of *On the sustainable development of cement*.

White Rose Research Online URL for this paper: http://eprints.whiterose.ac.uk/149609/

Version: Accepted Version

## **Proceedings Paper:**

Hanein, T. orcid.org/0000-0002-3009-703X, Provis, J. and Kinoshita, H. (2018) On the sustainable development of cement. In: Proceedings, Young Researchers Forum IV - Innovation in Construction Materials. Young Researchers' Forum IV - Innovation in Construction Materials, 09 Apr 2018, Northumbria University, Newcastle, UK.

© 2018 The Author(s).

#### Reuse

Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

#### **Takedown**

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



# On the Sustainable Development of Cement

T. Hanein, J. L. Provis, and H. Kinoshita Department of Materials Science and Engineering, The University of Sheffield, Sheffield S1 3JD, UK

#### **ABSTRACT**

Cement is the most manufactured product on earth. Unfortunately, the manufacture of cement is accompanied by the emission of carbon dioxide gas. Among all manufacturing industry sectors in the UK, the cement industry is the largest CO<sub>2</sub> emitter and these emissions are damaging our planet. The sustainable development of cement will allow future generations to develop without being compromised by the cement industry. This work identifies some of the routes to reducing the environmental burden of the cement industry.

#### 1. INTRODUCTION

Portland cement (PC) has been used over the past century as the binder of almost all our infrastructure. Approximately four billion tons of PC is produced globally every year (Jewell and Kimball, 2015) making it the second most consumed commodity in the world; surpassed only by water. Due to the high demand for cement, its production is responsible for approximately 8% (Olivier et al., 2016) of global anthropogenic CO<sub>2</sub> emissions that are damaging our planet. Climate change mitigation is one of the major global challenges today, and the sustainable development of the cement industry is an essential part of this.

Calcium oxide is a key constituent of PC clinker obtained from is Approximately two thirds (by volume) of the CO<sub>2</sub> emissions associated with traditional cement manufacture are generated from the embodied carbon liberated upon ignition of the CaCO<sub>3</sub> sources used such as limestone; the remainder are mainly from the combustion of fossil fuels required for the pyro-processing of the raw materials. In addition to direct process efficiency improvements, several avenues have been explored to reduce the environmental carbon burden of cement manufacture including: the (1) use of supplementary cementitious materials (SCMs). (2) the adoption of alternative raw materials, (3) the use of alternative fuels, (4) carbon capture and storage, and (5) the formulation of alternative lowcarbon binders. The former three have already been applied by the cement industry, as they have been relatively easy to implement. However, the scope for further improvement using alternative raw materials and SCMs is limited due to the limited availability of alternative raw materials where a significant fraction of the necessary calcium for the clinker exists in a de-carbonised form, and by the limited availability of SCMs that require only minor or no processing (Gartner and Hirao, 2015). The use of alternative fuels has been found to mainly improve the economic performance of cement production rather than significantly reducing its negative environmental effects (Galvez-Martos and Schoenberger, 2014). Carbon capture and storage is difficult to implement at scale as it is technologically immature, will require major capital investments, and is currently uneconomical without supporting governmental regulations to incentivise its adoption. The formulation of alternative low-carbon binders is one of the most auspicious paths to reducing the CO<sub>2</sub> emissions associated with cement manufacture.

### 2. ALTERNATIVE "LOW-CARBON" BINDERS

most promising and semi-established alternatives to PC are calcium sulfoaluminate (C\$A) based cements and geopolymer cements. C\$A cements are already produced in the world today (most notably in China) and used in both structural and non-structural applications; however, they are mainly used today for special applications. They have potential for widespread use in general construction as their manufacture offers a reduction in CO<sub>2</sub> emissions of approximately 30% when compared to PC due to their lower energy, temperature, and limestone requirements (Hanein et al., 2018). The production of C\$A-based cement at industrial scale requires minimal new capital investment as they can be produced in existing cement kiln configurations with only minor modifications (Hanein et al., 2016, Hanein et al., 2017a). C\$A cements also have the advantage that cheaper high-sulfur containing fuels or "sour" fuels can be used in their pyro-processing as the sulfur will be incorporated into the clinker. Additionally, C\$A cement can achieve a strength within a few days that requires 28 days for PC. The main hindrance to the production of C\$A-based cements at industrial scale in Europe is the cost of the additional alumina source required to form the calcium sulfoaluminate phase: ye'elimite (Hanein et al., 2018). However, the use of high aluminacontaining clays and/or alumina-containing wastes or by-products instead of the more expensive bauxite mineral for the mass production of C\$A-based cements are proven alternatives.

The performance of geopolymer cements is equal to or better than the performance of PC in numerous applications. Producing geopolymer cements from fly ash and slag does not require pyro-processing and therefore does not produce CO<sub>2</sub> emissions or require major capital investment. However, producing the necessary alkali activator does lead to the emission of CO<sub>2</sub>. The availability of fly ash and slag is limited in many OECD countries; therefore, in these places the long-term adoption of geopolymer cement as an alternative to PC will rely on a shift to other aluminosilicate materials such as metakaolin, which does require heat treatment for its production (de-hydroxylation of kaolin). The cost (environmental and monetary) of the required activator is a significant challenge larger-scale geopolymer deployment. However, the production of NaOH via sustainable carbon-neutral energy sources is a promising proposition for producing alkaline activators at industrial scale for geopolymer cements (Rethinking Cement, 2017).

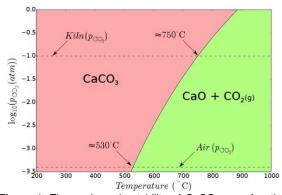
# 3. DEVELOPING THE PORTLAND CEMENT PRODUCTION PROCESS

PC is by far the most trusted, developed, and understood material in global construction. Modern and up-to-date PC plants boast an energy efficiency of 50 - 60% (European Commission, 2013). Some of the existing PC plants today are less efficient as they use older technologies, and updating these plants to use the best available techniques and the most efficient equipment is one direct way of reducing their fuel-derived carbon footprint. However, in many cases this may not be economical, and thus realistic, due to the residual "lifetime" of the plant's quarry.

As there is little room for inexpensive improvement in the modern PC plant configurations, a research avenue that requires substantial exploration is creating a novel low-carbon process for the manufacture of PC. Research avenues on the manufacture of PC discussed here include using electric furnaces powered from sustainable energy sources, and lowering the temperature of cement manufacture.

Sustainable energy generation is undergoing rapid development; carbon-based fuels are considered to be in limited supply, and will eventually be depleted. Thus, industry should consider a shift towards using sustainable sources to power chemical processes. Using sustainable energy sources for the manufacture of cement implies the need for indirectly fired electric furnaces. Researchers have been making cement in electric

powered furnaces for decades; so, it is well known that the manufacture of PC is feasible in the absence of a combustion atmosphere. In an electric furnace, the temperature and energy required for the calcination of CaCO<sub>3</sub> would decrease as the atmosphere would have a lower CO<sub>2</sub> partial pressure; thus, promoting the decarbonisation of CaCO<sub>3</sub> (see Fig. 1). Utilising electric furnaces will also allow for easier and more economical capture and/or sequestration of CO2 as flue gas would have a higher CO<sub>2</sub> concentration. Another advantage of using electric furnaces for cement manufacture is the reduction of the associated NO<sub>x</sub> emissions, as excess air for combustion of fossil fuel will not be required. The use of electric kilns powered from sustainable sources should also be considered for the lime and magnesia cement industries. To develop this concept, reactive heat transfer models are necessary and a systematic study quantifying its benefits is required.



**Figure 1.** Thermodynamic stability of  $CaCO_3$  as a function of temperature and  $CO_2$  partial pressure calculated from data taken from McBride et al., 2002. The dashed lines represent the  $CO_2$  partial pressures in air and in a conventional PC kiln. Note that the  $CO_2$  concentration in the pre-calciner will be higher due to the  $CO_2$  evolving from calcination.

The advantages of producing cement at lower temperatures include the requirement for less traditional carbon-based fuels and the capability of using alternative fuels that have lower flame temperatures. An already industrialised method to reducing the clinkering temperature of PC is the use of mineralisers such as CaF2 where the fluorine allows for the entropy stabilisation of alite (the major phase in PC clinker) at a temperature approximately 200°C lower than is traditionally used (Shame and Glasser, 1987). More recent research studies have focused on reducing the temperature of cement production even further via molten salt syntheses of cement compounds (Photiadis et al., 2011, Hanein et al., 2017b). One hurdle in producing cement via molten salt syntheses is finding a cheap localised salt source. The cheapest salts with appropriate melting temperatures are chloride salts; chloride is well known to be damaging to reinforced concrete as it promotes steel corrosion (Galan and Glasser, 2015), and so introducing more chloride into the system may not be welcomed by the construction industry unless complete separation of the salt from the final product is ensured. Also, due to the energetics of alite (the major phase in PC) formation, it may not be possible to produce it at much lower temperatures than is already practiced. However, there exists the potential to produce additives to PC or other types of cement via molten salt syntheses.

Modern cement pyro-processing is performed in a pre-calciner rotary kiln configuration where the calcination of limestone is followed by clinkerisation. However, if these two parts are decoupled, advantages can be realised. Firstly, it would be easier and more economical to capture and/or sequester CO<sub>2</sub> from the front end (where calcination occurs) if the process is de-coupled as the flue gas would have a higher CO<sub>2</sub> concentration (no kiln combustion air). Also, other advanced process technologies can be adopted to replace part or all of the cement manufacturing process.

#### 4. DISCUSSION

The two types of alternative binders with the greatest potential to replacing PC are calcium sulfoaluminate and geopolymer cements. However, as different cements and hybrids thereof have different properties, it could be more beneficial to shift to using application-specific cements rather than looking for a "one size fits all" solution. Market uptake of alternative binders to be used in general construction applications is hindered by the availability of raw materials and, in some cases, the lack of standardisation which delays the subsequent use of these new binders by the construction industry.

If the construction industry is to maintain PC as a binder for general construction, new and exciting ways of thinking are necessary to develop a novel low-carbon PC production process and mitigate the environmental burden of the cement industry. One idea is the use of electric furnaces powered from sustainable sources.

The construction industry has a necessarily conservative mind-set due to the enormous quantities of materials that must be processed, and the very high consequences of technical failure of infrastructure – so they are not easily convinced to take up new technologies. Governments around the world have already implemented CO<sub>2</sub> taxation and the cost of emitting CO<sub>2</sub> is on the rise. Therefore, the cement industry will eventually have no choice but to act further on its environmental burden and the avenues discussed here should be considered.

#### **REFERENCES**

European Commission, 2013. JRC Reference Report on Best Available Techniques in the

- Cement, Lime and Magnesium Oxide Manufacturing Industries.
- Galan, I., Glasser, F. P., 2015. Chloride in cement. Advances in Cement Research 27(2): 63-97.
- Galvez-Martos, J.L., Schoenberger, H., 2014. An analysis of the use of life cycle assessment for waste coincineration in cement kilns. Resources, Conservation and Recycling, 86:118-131.
- Gartner, E., Hirao, H., 2015. A review of alternative approaches to the reduction of CO<sub>2</sub> emissions associated with the manufacture of the binder phase in concrete. Cement and Concrete Research, 78:126-142.
- Hanein, T., Galan, I., Elhoweris, A., Khare, S., Skalamprinos, S., Jen, G., Whittaker, M., Imbabi, M. S., Glasser, F. P., and Bannerman, M. N., 2016. Production of Belite Calcium SulfoAluminate cement using sulfur as a fuel and as a source of clinker sulfur trioxide: Pilot kiln trial. Advances in Cement Research, 28(10):643-653.
- Hanein, T., Galan, I., Glasser, F. P., Skalamprinos, S., Elhoweris, A., Imbabi, M. S., and Bannerman, M. N., 2017a. Stability of ternesite and the production at scale of ternesite-based clinkers. Cement and Concrete Research, 98C: 91–100.
- Hanein, T., Provis, J.L., Nyberg, M., Quintero Mora, N. I., Tyrer, M., Maries, A., Kinoshita, H., 2017b. Molten salt synthesis of compounds related to cement. 1st International Conference on Cement and Concrete Technology, Muscat, Oman.
- Hanein, T., Galvez-Martos, J. L., Bannerman, M. N., 2018. Carbon footprint of calcium sulfoaluminate clinker production. Journal of Cleaner Production, 172:2278-2287.
- Jewell, S., Kimball, S.M., 2015. Mineral Commodity Summaries. US Department of the Interior: US Geological Survey.
- McBride, B.J., Zehe, M.J., Gordon, S., 2002. NASA Glenn Coefficients for Calculating Thermodynamic Properties of Individual Species. NASA TP-2002-211556.
- Olivier, J.G.J., Janssens-Maenhout, G., Muntean, M., Peters, J.A.H.W., 2016. Trends in Global CO<sub>2</sub> Emissions: 2016 Report. PBL NEAA and ECJRC IES
- Photiadis, G. M., Maries, A., Tyrer, M., Inman, D., Bensted, J., Simons, S., Barnes, P., 2011. Low energy synthesis of cement compounds in molten salt. Advances in Applied Ceramics 110(3): 137-141.
- Rethinking Cement. Beyond Zero Emissions Technical Report. Available at: http://bze.org.au/rethinking-cement-plan/.
- Shame, E.G., Glasser, F.P., 1987. Stable Ca<sub>3</sub>SiO<sub>5</sub> solid solutions contaning fluorine and aluminium made between 1050 and 1250 ℃. Transactions and Journal of the British Ceramic Society 86(1): 13-17.