ABSTRACT

The production of Portland cement (PC) is associated with many environmental challenges including the air pollution and devastation in land and resources. In addition, the cement industry is one of the highest industrial emitters of CO_2, accounting for ~7% of man-made CO_2 emissions, which contributes significantly to the climate change. Various measures have been proposed or implemented to reduce the carbon footprint of the cement industry such as improving the energy efficiency, use of renewable energy, and carbon capture and storage technologies. One of the promising measures is the development of sustainable cements, which can be achieved via two main pathways: (i) partial PC replacement with industrial by-products and wastes and (ii) new cement formulations based on different chemistry with lower environmental impacts. Two promising sustainable cements are alkali-activated slag cements (AAS) and MgO-based cements. However, AAS suffers from large drying shrinkage and the use the caustic alkalis. In addition, previous studies have demonstrated that the properties of the MgO-based cements are highly dependent on the characteristics of the MgO used.

Recently, the combination of reactive MgO and several supplementary cementitious materials (SCMs) has been proposed as a series of novel reactive MgO cements which not only give technical advantages, but also environmental merits compared to PC. Furthermore, MgO calcined between 900 and 1300 °C showed great potential in mitigating the shrinkage problem for the dam concrete application in China. Nevertheless, there is a dearth of knowledge about the hydration mechanisms between reactive MgO and different SCMs and the effect of reactive MgO on the properties of AAS. Therefore, the current study is dedicated to develop novel reactive MgO-based cements with SCMs and to explore the role of reactive MgO in AAS cements.

Reactive MgO is usually calcined at 700-1000 °C and possesses higher reactivity, larger surface area than those calcined at higher temperatures and its characteristics vary considerably depending on its source and calcination conditions. It is expected that the performance of reactive MgO-based cements would vary notably when using reactive MgO with different characteristics. Therefore, in the first part of this thesis, a thorough characterisation of 14 commercial reactive MgOs was performed in terms of chemical reactivity, particle size, textural properties, hydration rate, pH value of the hydration products

and microstructure. Based on the understanding of the relationships between different properties, the reactive MgOs were divided into 3 categories, namely, high reactivity, medium reactivity and low reactivity MgO.

Furthermore, two novel reactive MgO-based binary cements, namely, reactive MgO-microsilica cement and reactive MgO-slag cement were studied in terms of their mechanical and hydration properties. Findings showed that the replacement of microsilica by reactive MgO at 50 wt% achieved ~16 MPa at 56 days. The formation of magnesium silicate hydrate (M-S-H) has been confirmed by various techniques such as X-ray diffraction (XRD), thermogravimetric analysis (TGA) and secondary electron microscopy (SEM). In terms of reactive MgO-slag cement, it was found that the ground granulated blastfurnace slag (GGBS) used can be successfully activated by reactive MgO with contents up to 15 wt% and the blends could achieve ~40 MPa at 28 days. The main hydration products were found to be calcium silicate hydrate (C-S-H) and hydrotalcite-like phases, the latter of which was believed to result in a less porous matrix and improved strength. The reactive MgO-slag cement was then investigated for heavy metal immobilisation and showed improved pH buffering capacity, better mechanical and immobilisation performance than the corresponding $Ca(OH)_2$-GGBS paste. In addition, the effect of the characteristics of MgO on the properties of the two cement systems was discussed.

In the last section, three reactive MgO-based ternary cement systems, namely, reactive MgO-CaO-slag, reactive MgO-waterglass-slag and reactive MgO-sodium carbonate-slag cement, were investigated in terms of their mechanical, drying shrinkage and hydration properties. Findings showed that 5% of CaO impurity in MgO could significantly increase the pH of the pore solution and consequently the slag dissolution degree, resulting in higher early strength of reactive MgO-slag blends. In the reactive MgO modified AAS cements (MAAS), it was found that MgO with high reactivity was more effective in improving the early strength and reducing the early drying shrinkage, while MgO with medium reactivity took effect at a later age. The reactivity and content of MgO has a notable effect on the performance of the MAAS. It was concluded that reactive MgO has great potential to mitigate the shrinkage problems of AAS and serve as a promising sustainable activator for GGBS.