ABSTRACT

As the most widely used construction material in the world, the global production of Portland cement was 4.1 billion tonnes in the year of 2015. Due to the intensive energy demand during the manufacturing processes, the manufacture of PC was estimated to be responsible for 5-7% of worldwide man-made emissions of CO_2 along with other pollutants. Since the importance of the sustainability credentials of construction are becoming more important, it is in urgent need to identify more sustainable binders which have a gentler impact on the environment while maintaining sufficient in-service performance. Magnesia-based cement is a promising alternative to PC due to its lower energy demand during production and its potential to absorb CO_2 during strength development. However the widely industrial application of new types of cement requires sufficient understanding of the nature of the material through abundant experiments and accurate modelling works.

In terms of the modelling work, the microscale models in cement study have been focused on PC and they may not be fully applicable to other types of cement such as magnesia-based cement. The microstructure development process of magnesia-based cement is more difficult to describe than that of Portland cement due to the local solute concentration difference in capillary pores caused by the carbonation process. As a result, the mainstream techniques to model the microscale phase distribution development of Portland cement cannot be fully adopted in the case of simulating magnesia-based cement regardless of the changing physical and chemical parameters. A novel microscale model was constructed through this PhD work based on the dissolution-precipitation theory in the field of mineral crystallization and the discrete description of the diffusion-reaction system associated with lattice Boltzmann method.

A 3D digitized particle packing program was written to provide the microscale model with adjustable initial solid phase boundary conditions with a phase fraction ranging from 0 to 0.7. It was found that the peak coordination number of random loose packing was simulated to be 4 and the peak coordination number of random close packing was simulated to be 6. Packing simulation with normal distributed particle sizes was conducted and it was found that the packing fraction of random loose packing and random close packing increased with raised standard deviation when the standard deviation was above 0.1.

A 3D surface dissolution-precipitation simulation program was coupled with a 3D diffusion-reaction simulation program to simulate the microstructure formation process of the

magnesia-based cement based on the homogeneous reaction assumption. The 3D simulation program is able to simulate the development of the discrete solid phase and liquid phase distribution of a 100^3 μm^3 cubic MgO-based cement microstructure with a length mapping of 1μm per lattice against computational time steps. It was numerically observed that the capillary porosity reduction increased with loose packing configuration due to the high capacity of the system to form precipitation solid phases. Samples with smaller particle size showed an accelerated development of degree of dissolution and degree of precipitation due to the increment in specific surface area of solid phases. Inert particles served as crystallization seeds for the precipitation process and a reduced inert particle size accelerated the porosity reduction due to increased specific surface area for precipitation. Reduced capillary pore size accelerated the reduction of the porosity due to increased specific surface area for dissolution and precipitation.

Through the numerical percolation analysis of the digitized samples, the depercolation threshold was identified to be within the range of 9% to 10% in this study. In the formation factor development analysis of the digitized samples, Archie's law with the tortuosity of 1 and cementation exponent of 1.56 was properly met by the simulation results. The cement surface microstructure development simulation based on the heterogeneous reaction assumption indicated that local rapid solid precipitation phase formation would raise the global depercolation threshold and slow down the global rate of precipitation.

The initial volumetric content of magnesia for the most efficient usage was calculated to be 15%, 11.3% and 5.4% for 100% volume coverage for the formation of nesquehonite, hydramagnesite and lansfordite, respectively. For the percolation maintenance purpose, the initial volumetric content of MgO for the most efficient usage was calculated to be 13.5%, 10.1% and 4.9% for the formation of nesquehonite, hydramagnesite and lansfordite, respectively. In the mesoscale bulk density development with water/cement ratio of 0.78 and 100% MgO, increment of bulk density of 0.0598 g/cm^3 to 0.0717g/cm^3 was simulated, which was similar to the previous experimental observation.

Though still not fully developed, the model of this work is able to simulate the microstructure development of MgO-based cement with the assumption of homogeneous reaction and single precipitation product. Due to its mechanism-based nature, it has the potential to be part of the universal simulation scheme for all types of cement.