# Development of Low-pH Magnesia-Bearing Cements for the Immobilisation of Radioactive Waste

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A dissertation submitted for the degree of
Doctor of Philosophy
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January 2017

# ABSTRACT

Technologies employing radionuclides are indispensable to modern society. However, these activities generate hazardous radioactive waste, which require proper control and management. Although solidification/stabilisation in cementitious binders is one of the best-known methods for conditioning of contaminants, the overall efficiency of the process is compromised by inadequacies arising from the traditionally used Portland cement (PC). The limited efficiency of this binding system is primarily a consequence of its high alkalinity, which yields very aggressive leachates and represents a serious setback within the multi-barrier concept governing the design of nuclear repositories. Hence, with the objective of address this issue, this research has focused on developing binding systems with lower or no content of PC. Two novel cementitious systems: Reactive Magnesium Oxide (MgO) and Magnesium Potassium Phosphate Cements (MKPC), including silica-fume (SF) and fly-ash (FA) as supplementary materials and boric acid as a cement setting retarder, were studied. These systems, classified as low-pH cements, amongst other advantages, present pore waters with $pH \leq 11$ and are potentially suitable for the design of safer and more sustainable waste forms.

In general, cements are very complex chemically. Several factors operate in parallel to promote specific reactions that ultimately define the suitability of matrices. Segregation and control of these factors can be challenging and often unmanageable when studies are carried out by laboratory experiments. Hence, in the first part of this thesis, a speciation-solubility model to simulate the hydration of blends was developed using the software PHREEQC. This geochemical software applies thermodynamic principles and has been largely used in analyses of environmental impacts and migration of contaminants. The developed speciation-solubility model executed well the hydration of a variety of systems, i.e. PC, MgO, PC/SF, PC/MgO, MgO/SF, MgO/$KH_2PO_4$, PC/MgO/SF, MgO/$KH_2PO_4$/FA and MgO/$KH_2PO_4$/$H_3BO_3$, with satisfactory agreement with the literature. Investigations confirmed the inaptness of PC as binder for radioactive waste, since that the average pH of pore waters was 13.5, controlled by soluble alkalis. Analyses also identified that the composition of the starting materials affected the properties of all blends considerably. Particularly for systems containing magnesia, the presence of CaO impurities promoted the formation of C-S-H in addition to brucite, increasing the pH of pore waters. Simulations proved the great potential of SF as supplementary material to achieve low-pH cements. While MgO was unable to displace portlandite in PC/MgO systems, pozzolan reactions in PC/SF and PC/MgO/SF consumed $Ca(OH)_2$ and effectively reduced the pH of pore waters. SF also supported the formation of M-S-H in MgO/SF and PC/MgO/SF systems. Investigations revealed that the formation of magnesium silicate hydrates in MgO cements was highly favorable to lower pH of pore waters. Lastly, analyses demonstrated that brucite and k-struvite were the main hydration products of MKPC when the $KH_2PO_4$ was the phosphate source. Although the addition of $H_3BO_3$ did not alter the solid phase composition, it reduced the pH of pore waters of MKPC significantly. On the other hand, neither the pH nor solid phase assemblages were altered by the addition of FA. Therefore, subsequent studies focused on MgO and MKPC represented by the ternary formulations MgO/PC/SF and $MgO/KH_2PO_4/H_3BO_3$.

In the second phase of this thesis, the developed and verified speciation-solubility model was employed in the acquisition of data required for the statistical optimisation of formulations. Assessments were performed using the software Minitab® and results allowed the construction of mathematical equations describing the optimal response (pH of pore waters) in function of proportions and relevant interactions between the cement constituents. Analyses revealed that while the average pH of pore waters of PC was 13.5, a wide range of MgO and MKPC formulations suitably promoted $10.5 < pH < 11$. This assortment allows flexibility for accommodating further changes caused by external factors identified, such as the presence of CaO impurities, and the chemical composition of the radioactive waste and the groundwater present in the final repository.

The final phase of investigations combined the speciation-solubility model within a mixing tank approach represented by an unary cell to simulate waste forms, evaluate degradation when systems were exposed to pure water and groundwater flows and access the leaching of uranium (U(IV) and U(IV)) from the selected compositions. Studies also demonstrated that the durability of MgO and MKPC was at least 3.5 times higher when compared to PC exposed to pure water. Furthermore, analyses of leaching process indicated that the persistence of saturation states for solubility-limiting phases of uranium ($CaUO_4$, $USiO_4$ and uranophane) in systems based on PC was 66% and 76% shorter when compared to MgO and MKPC, respectively. Overall studies performed in this thesis suggested that, within the parameters evaluated, the global performance of MgO and MKPC as binders for radioactive waste was fairly superior to PC.