International Workshop on Innovation in Low-carbon Cement & Concrete Technology 21-24 September 2016, University College London, U.K. Paper number 17

# Magnesia-bearing Materials for Challenging Infrastructure and Environment

Abir Al-Tabbaa, Fei Jin Dept. of Engineering, University of Cambridge, UK

Yun Bai Dept. of Civil, Environ &Geomatic Engineering, UCL, UK

Jueshi Qian Dept. of Building Material Engineering, Chongqing University, China

Liwu Mo

College of Material Science and Engineering, Nanjing Tech University, China

ABSTRACT: Our infrastructure and environment face unprecedented challenges in addressing a low carbon future with limited natural resources, expanding population, increased pollution and climatic uncertainties. Adaptation and innovations must therefore play a vital role in addressing the anticipated wide ranging complex scenarios ahead. The environment in which construction materials will need to function will become far more complex and aggressive and hence a fundamental revaluation of the most appropriate materials for future infrastructure and environment will be required in order to tackle those challenges. This paper focuses on a class of construction materials, both old and new, based on magnesia (MgO). They include a wide range of materials from those that contain MgO as a small additive to those which solely consist of MgO. They include concrete with MgO as an expansive additive, pervious concrete, alkali-activated cements, magnesium phosphate cements, carbonated products, stabilising additives for ground improvement, self-healing additives, carbon capture and storage materials and binders for waste

and contaminated land remediation. Those materials and products offer a range of technical and sustainability benefits for a range of structural, geotechnical and environmental applications. The paper highlights the applications and benefits that would be achieved with magnesia-bearing construction materials.

Keywords: durability, environment, infrastructure, MgO, production

#### INTRODUCTION

With unprecedented population growth, the world is becoming a place that is more crowded, more consuming, more polluted and more connected than any time in history and has led to significant over-exploitation of raw materials and excessive emissions of greenhouse gases. The number of megacities has increased sharply, particularly in developing countries like China leading to energy crises and environmental pollution. For example, China experienced severe energy shortages in early 2008 and in 2014; China's environmental ministry stated that almost 20% of the country's farmland was dangerously polluted. Hence we face significant challenges moving forward in terms of environmental deterioration, renewable energy exploitation and megacity infrastructure, that will impact significantly on future construction practices and in particular construction materials use and applications.

Addressing these challenges will rely on technologies made possible by innovations in materials, which play a significant role in providing the tools required in designing sustainable, resilient and secure construction. Portland cement (PC), currently the backbone of most construction, is the most widely used cement and its technical and durability credentials are unparalleled. However, it is responsible for significant anthropogenic  $CO_2$  emissions and huge negative environmental impacts. It also has specific technical drawbacks and as a result will be unable to meet many of the stringent technical performances and long-term durability demands associated with the challenges listed above. Significant efforts around the world have been dedicated to the development of more sustainable PC, more sustainable alternatives and more resilient cements for specific applications. This paper presents an overview of magnesia and its specific credentials in a series of magnesia-bearing materials that could bring significant benefits for our future environment and infrastructure.

## **MAGNESIA-BEARING MATERIALS**

The last two decades has witnessed an increasingly significant international interest in the development and applications of magnesia-bearing materials<sup>[1]</sup>. This is fuelled by a number of factors: (i) increased demands for alternative cements to PC with enhanced durability and reduced environmental impacts, (ii) sequestration of  $CO_2$  in Mg-rich minerals and wastes as part of the global carbon capture and storage strategy and (iii) knowledge transfer of China's unique expertise and successful practice of magnesia (MgO) in large mass concrete dams.

The fundamental characteristics of MgO provide its unique performance upon production, hydration, carbonation, and other reactions with acid phases with wide ranging potential applications in waste treatment and cementitious composites. It has a higher propensity for mixing with waste and is less sensitive to impurities compared to PC and is hence far more amenable to

incorporation into waste-based materials. Magnesium hydroxide (MH, Mg(OH)<sub>2</sub>), the hydration product of MgO, is far less soluble than portlandite and its pH is stable in the long-term imparting enhanced chemical durability. The formation of MH is expansive with ~2 fold solid volume increase, which has been employed in China to compensate shrinkage cracking of PC in large mass concrete dams<sup>[2]</sup>. MH is also chemically stable at high temperatures (decomposing at ~400  $^{\circ}$ C) and is hence more resilient in higher temperature environments. The equilibrium pH of MH, lower than that of portlandite, is around the optimum value for the precipitation of the most common heavy metal contaminants and the high internal porosity renders it an excellent adsorbent for both organic and inorganic pollutants. Moreover, the reaction of MgO with silica & alumina phases and acid phosphates and carbonation reactions with CO<sub>2</sub> lead to the formation of different Mg-bearing products, e.g. magnesium silicate hydrate (M-S-H), hydrotalcite-like phases, struvites, hydrated magnesium carbonates (HMCs) such as nesquehonite, dypingite, hydromagnesite, and magnesian calcites, contributing to denser microstructure and enhanced mechanical strength and resistance to chemical attack and corrosion as well as enhanced contaminant immobilisation capacity. It was also realised recently that the hydration and expansion properties of MgO are also far more designable, with adjustments of their microstructure through changes in the calcination process and material sources, making it an extremely versatile material. The following magnesia-bearing materials have been proposes/trialled: (i) MgO expansive cement<sup>[3]-[6]</sup>; (ii) Carbonated MgO concrete products<sup>[7], [8]</sup>; (iii) MgO-based self-healing materials<sup>[9]-[11]</sup>; (iv) MgO-based binders, soil stabilising additives and sorbents<sup>[12]-[16]</sup>; (v) MgO-modified alkali-activated and waste-based cements<sup>[17]–[19]</sup>; (vii) Magnesium phosphate cements<sup>[20]–[22]</sup>.

MgO is globally produced at a range of 20 Mt/year, mainly from the calcination of magnesite in China, from "high grade" magnesite mines and holds half the world's reserves. The remaining 20% are produced from brine, seawater and from chemical precipitation. Although the current production routes of MgO are not particularly sustainable, there are significant opportunities for the sustainable production of MgO from both low-grade magnesite, dolomite and Mg-rich wastes as well as from reject brines<sup>[1]</sup>. Fig. 2 shows a research roadmap for resilient and sustainable magnesia-bearing materials.



Fig. 2 Research roadmap for resilient and sustainable magnesia-bearing future construction materials

## CONCLUSIONS

This paper presents an overview of the features of magnesia and its application in a class of magnesia-bearing materials that have the potential to make a significant contribution to our future infrastructure and environment. These include: expansive additives, carbonated products, self-healing materials, binders and sorbents, soil stabilisation additives, alkali-activated and waste-based cements, and magnesium phosphate cements. All these materials are being extensively investigated by the authors and their research groups both independently and in collaboration to realise their appropriate applications. The technical and environmental advantages already seen clearly demonstrate a superior performance in terms of enhanced mechanical performance, enhanced durability, enhanced hydraulic properties, enhanced microstructure and generally enhanced performance in aggressive environments.

## ACKNOWLEDGEMENTS

Financial support from UK EPSRC and Royal Academy of Engineering and China National Nature Science Foundation of China are much appreciated.

## REFERENCES

- [1] A. Al-Tabbaa, *Reactive magnesia cement. Book chapter in Eco-efficient concrete: edited by Pacheco-Torgal et. al.* Woodhead, 2013.
- [2] L. Mo, M. Deng, M. Tang, and A. Al-Tabbaa, "MgO expansive cement and concrete in

China: Past, present and future," Cem. Concr. Res., vol. 57, pp. 1-12, 2014.

- [3] W. Lau, L. Mo, A. Al-Tabbaa, and J. Stehle, "Overview of the application of MgO for concrete shrinkage reduction in China: fundamental concept and state-of-the-art research," in *1st Concrete Innovation Conference (CIC)*, 2014.
- [4] W. Lau, L. Mo, A. Al-Tabbaa, and J. Stehle, "Expansion properties of two different reactivity MgOs produced from magnesite and seawater," in 34th Cement and Concrete Science Conference, 2014, pp. 197–200.
- [5] L. Mo, M. Liu, A. Al-Tabbaa, and M. Deng, "Deformation and mechanical properties of the expansive cements produced by inter-grinding cement clinker and MgOs with various reactivities," *Constr. Build. Mater.*, vol. 80, pp. 1–8, 2015.
- [6] L. Mo, M. Liu, A. Al-Tabbaa, M. Deng, and W. Yuk, "Deformation and mechanical properties of quaternary blended cements containing ground granulated blast furnace slag, fly ash and magnesia," *Cem. Concr. Res.*, vol. 71, pp. 7–13, 2015.
- [7] L. Mo and D. K. Panesar, "Effects of accelerated carbonation on the microstructure of Portland cement pastes containing reactive MgO," *Cem. Concr. Res.*, vol. 42, no. 6, pp. 769–777, Jun. 2012.
- [8] L. Mo and D. K. Panesar, "Accelerated carbonation A potential approach to sequester CO2 in cement paste containing slag and reactive MgO," *Cem. Concr. Compos.*, vol. 43, no. 0, pp. 69–77, Oct. 2013.
- [9] T. Qureshia, A. Kanellopoulosa, and A. Al-Tabbaaa, "Enhancing Autogenous Self-healing of Portland Cement through Partial Substitution with Expansive Minerals (in press)," *Cem. Concr. Res.*
- [10] A. Kanellopoulos, T. Qureshi, and A. Al-Tabbaa, "Encapsulated mineral precursors for self-healing cement based composites," *Constr. Build. Mater.*, vol. Accepted, 2015.
- [11] R. Alghamri and A. Al-Tabbaa, "Self-healing Concrete by Using MgO Based Pellets Enclosed by PVA Film Coating," in *Proceedings of the 5th International Conference on Self-Healing Materials*, 2015.
- [12] F. Jin and A. Al-Tabbaa, "Evaluation of novel reactive MgO activated slag binder for the immobilisation of lead and zinc," *Chemosphere*, vol. 117, pp. 285–294, Dec. 2014.
- [13] F. Jin, F. Wang, and A. Al-Tabbaa, "Three-year performance of in-situ solidified/stabilised soil using novel MgO-bearing binders," *Chemosphere*, vol. 144, pp. 681–688, Feb. 2016.
- [14] F. Wang, H. Wang, and A. Al-Tabbaa, "Time-dependent performance of soil mix technology stabilized/solidified contaminated site soils," *J. Hazard. Mater.*, vol. 286, pp. 503–508, 2015.
- [15] K. Gu, F. Jin, A. Al-Tabbaa, B. Shi, C. Liu, and L. Gao, "Incorporation of reactive magnesia and quicklime in sustainable binders for soil stabilisation," *Eng. Geol.*, vol. 195, pp. 53–62, 2015.
- [16] D. O. Connor and A. Al-Tabbaa, "Preliminary observations on shrinkage of cementbentonite barrier wall materials and its compensation by reactive magnesia addition," in *7th International Congress on Environmental Geotechnics*, 2014.
- [17] A. F. Abdalqader, F. Jin, and A. Al-Tabbaa, "Characterisation of reactive magnesia and sodium carbonate-activated fly ash/slag paste blends," *Constr. Build. Mater.*, vol. 93, pp. 506–513, 2015.
- [18] F. Jin and A. Al-Tabbaa, "Strength and drying shrinkage of slag paste activated by sodium

carbonate and reactive MgO," Constr. Build. Mater., vol. 81, pp. 58-65, 2015.

- [19] F. Jin, K. Gu, and A. Al-Tabbaa, "Strength and drying shrinkage of reactive MgO modified alkali-activated slag paste," *Constr. Build. Mater.*, vol. 51, pp. 395–404, Jan. 2014.
- [20] J. Qian, C. You, Q. Wang, H. Wang, and X. Jia, "A method for assessing bond performance of cement-based repair materials," *Constr. Build. Mater.*, vol. 68, pp. 307– 313, 2014.
- [21] X. Wang, Z. Bai, D. Zhao, and F. Zhao, "Friction behavior of Mg–Al–CO3 layered double hydroxide prepared by magnesite," *Appl. Surf. Sci.*, vol. 277, pp. 134–138, 2013.
- [22] C. You, J. Qian, J. Qin, H. Wang, Q. Wang, and Z. Ye, "Effect of early hydration temperature on hydration product and strength development of magnesium phosphate cement (MPC)," *Cem. Concr. Res.*, vol. 78, pp. 179–189, 2015.