Nanotechnology Applications for Sustainable Cement-Based Products

L. Raki, J.J. Beaudoin, and R. Alizadeh

Abstract. Concrete is a macro-material strongly influenced by the properties of its components and hydrates at the nanoscale. Progress at this level will engender new opportunities for improvement of strength and durability of concrete materials. This article will focus on recent research work in the field of nanoscience applications to cement and concrete at the NRC-IRC. A particular attention will be given to nanoparticles and cement-based nanocomposites.

1 Introduction

Nanotechnology has been clearly identified as one of the key, cross-disciplinary areas of research for the next twenty years. Significant investments are being made in nanotechnology research in Canada and around the world. Recent studies have identified the construction industry as one of the major potential consumers of nanostructured materials [1]. Concrete is a composite material with structures ranging from nano to macro-scales. Its study represents a multidisciplinary area of research. Nanotechnology potentially offers the opportunity to further the understanding of concrete behaviour, to engineer its properties and to lower both the monetary and ecological cost of construction materials. The expected future economic and social benefits linked to the area of nanotechnology in general and in the field of concrete materials in particular will also have to include sustainability effects.

L. Raki
Institute for Research in Construction, National Research Council Canada
e-mail: `laila.raki@nrc-cnrc.gc.ca`

J.J. Beaudoin
Institute for Research in Construction, National Research Council Canada
e-mail: `jim.beaudoin@nrc-cnrc.gc.ca`

R. Alizadeh
Institute for Research in Construction, National Research Council Canada
e-mail: `rohallah.alizadeh@nrc-cnrc.gc.ca`

2 Controlled Release of Admixtures

Modern concrete is more than a simple mixture of cement, water, sand and aggregates. Today, more is demanded from concrete than ever before as it is being used in different forms and special applications such as high performance (HPC), self-levelling concrete (SLC), self-compacting concrete (SCC), ultra high performance concrete (UHPC) etc. These very high demand developments require the use of chemical admixtures in order to modify/control one or more properties of the fresh or hardened properties of concrete. The most used admixtures in cement and concrete include accelerators, set retarders, air entraining agents, superplasticizers and others. Today, chemical admixtures have become an integral part of the concrete technology and practice. Like drugs, chemical admixtures can produce side effects that can be beneficial or detrimental depending on the situation. A particular challenge of interest to concrete scientists is to optimize and maximize the use of supplementary cementing materials in high performance concretes. Dispersing agents such as superplasticizers are commonly used in these special concretes. There are, however, practical problems such as loss of workability with time that are controlled by interactions with cement components. Controlling the timing of the availability of an admixture in cement systems is essential for its optimal performance.

There have been a number of applications in cement and concrete technology where different means of controlling the effect of admixtures via a controlled release technique were used. A number of patents and research articles describe “encapsulation” procedures for delivery of liquids and solids. Encapsulation often relies on a soluble coating (gelatine or wax) to effect control. Mechanisms involve dissolution (coating), diffusion (membrane), desorption (porous materials), or mechanical removal (during mixing). A corrosion inhibitor, such as calcium nitrite, was dispersed by encapsulation in coated hollow polypropylene fibers [2] via an automated activation. Porous aggregates were also used to encapsulate antifreezing agents [3]. Porous solid materials were used to encapsulate oil well treating fluids [4]. Another method to control the release of chemicals in cement-based materials is by “intercalation-deintercalation”. A cement additive for inhibiting concrete deterioration was formulated as a mixture of an inorganic cationic exchanger: zeolite, and an inorganic anionic exchanger: hydrocalumite [5].

Admixtures are most often added at time of mixing, which is not necessarily optimum for the desired chemical effects. For instance, it is sometimes required to delay release of compounds such as superplasticizers, and other additives. Development of new materials for programmed delivery and control of admixtures in concrete and other materials presents a significant technological advance. Recent work from the authors [6, 7] examined means to control the timing of the release of chemical admixtures through their incorporation in nanoscale composite materials. More specifically, a series of new hydrocalumite derivatives were prepared by an anion exchange reaction of a synthetic precursor, hydrocalumite, and different model organic molecules used as admixtures in concrete technology. The technique consisted of intercalating an admixture into a hydrocalumite-like material and adding this composite to a cement-based mix. De-intercalation of the admixture could be actively programmed through controlled chemistry involving, for example, type of layered inorganic material, charge density, concentration of the admixture, and/or pH. A sulphonated naphthalene formaldehyde-based superplasticizer, Disal™, was used to produce the controlled release formulation (CaDisal) [7]. The effectiveness of Disal™ alone in controlling the slump-loss versus time characteristic was compared to that of the controlled release formulation CaDisal. Mini-slump measurements [8] indicated that the controlled release formulation provided a longer time for the superplasticizer to keep cement workability at a reasonable level after mixing [7]. Compressive strength measurements on mortar cubes at w/c=065 are shown in Figure 1. A general increase in strength with time for all mixes was observed. The mix with higher dosage of Disal (0.6% Disal) exhibited the lowest strength value in the series. The addition of the controlled release formulation 2.4% CaAl_Disal (2.4% CaDisal by mass of cement contains an equivalent amount of 0.3% Disal™) showed an increase with time and a higher value at 28 days (35.9Mpa) compared to other mixes including the control (33.4 Mpa). This later strength development could be due to slow hydration kinetics as a result of a slow release of the Disal, as shown by results from a separate study on hydration kinetics of C_3S systems with and without the controlled release formulation. The results obtained with this new composite additive confirmed that a slow release of the superplasticizer not only maintained the workability of the fresh mix but also improved the strength development of mortar samples. Further studies on long-term durability of concrete samples containing the controlled release composite are ongoing.

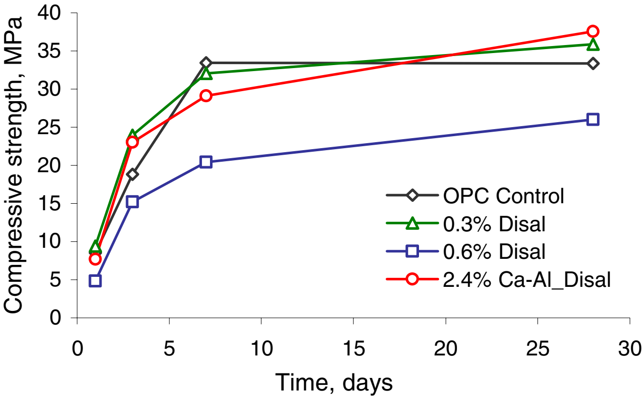

Fig. 1 Compressive strength for different mortar cubes (W/C=0.5)

3 C-S-H and C-S-H Composites

The primary binding agent in the hydrated Portland cement is a nearly amorphous material called Calcium-Silicate-Hydrate (C-S-H). It forms about 60% of the hydration products and is mainly responsible for important properties of hardened cement such as strength and volume stability. The nanostructure of C-S-H has been the subject of extensive debate for more than fifty years [9]. Improvement in our understanding of the nature of these hydration products would eventually result in better indentifying the underlying mechanisms in the mechanical and durability performance of concrete structures. It would also assist in engineering the nanostructure of cement-based systems and producing novel materials having superior characteristics.

A clearer image of the C-S-H nanostructure has emerged through the recent advancements in the analytical methods and experimental techniques [10-12]. Understanding of the relation between the chemical composition of C-S-H and its physical properties has certainly improved. The state of water in C-S-H is one of the most controversial issues in cement nanoscience. Although the pioneering model by Feldman and Sereda [13] is generally accepted for describing the microstructural behavior of hydrated Portland cement, further compelling evidence was recently presented in support of their layered model for C-S-H in cement paste [14]. Water molecules adsorbed on the surface of C-S-H or those located in the interlayer regions can significantly contribute to the mechanical behavior of hardened cement systems. Changes in the silicate structure or the interaction of calcium ions between the C-S-H sheets upon the removal of water may be responsible for variations in the mechanical response of C-S-H [15]. Cement paste and synthetic calcium silicate hydrate show analogous behavior in this regard.

As a part of the global efforts to improve the sustainability of concrete structures, investigations on the fabrication of organic/inorganic cementitious nanocomposites have shown early promise in achieving nanostructurally modified systems [16]. C-S-H based materials can be tailored at the nano level using several types of organic molecules in order to enhance the mechanical performance and volume stability. The organic moieties are interacted within the nanostructure of C-S-H during or after its preparation. There are indications that the produced nanocomposites have improved characteristics. It has been postulated that the organic guest molecules may possibly graft at defect sites of the silicate chain where bridging tetraherda is missing [17-19], intercalate into the interlayer space of the C-S-H [16], or form a covalent boding with the silicate structure [20, 21].

The extent of the interaction of organic molecules with the C-S-H nanostructure largely depends on the preparation procedure. X-ray diffraction and nuclear magnetic resonance spectroscopy are the primary tools that have resulted in obtaining more insight about the nature of the C-S-H based nano-hybrids. It has been shown using XRD that in some cases the organic substances can result in an increase of the 002 basal spacing of C-S-H up to as much as two times [22]. The ^{29}Si MAS NMR has revealed more details about the structural positions on the guest molecules with respect to the disordered crystal structure of C-S-H. The increase in the Q^2/Q^1 ratio determined from the NMR spectra following the interaction of several organic molecules (e.g. hexadecylmethylammonium, poly(ethylene glycol) and methylene blue) was attributed to the increased shielding of Q^1 silicate sites by the organic substances grafted in the defect locations on the silicate structure [17-19]. The effectiveness of the grafting process is dependent on the C/S ratio of the

C-S-H as the number of defect sites generally increases with C/S ratio >1.0. A schematic representation of the grafting mechanism is shown in Figure 2. It is speculated that the chemical stability of the polymer-modified C-S-H in aggressive environments is improved as the access to the interlayer region and the CH sheet is restricted by the organic molecules. True nano-hybrid systems can be prepared by the covalent bonding of the modified organic groups to the inorganic C-S-H base [11, 20, 21]. Polymers having silylated functions are introduced during the precipitation of C-S-H. The silylated group is incorporated into the silicate chain of the C-S-H and forms T silicon sites.

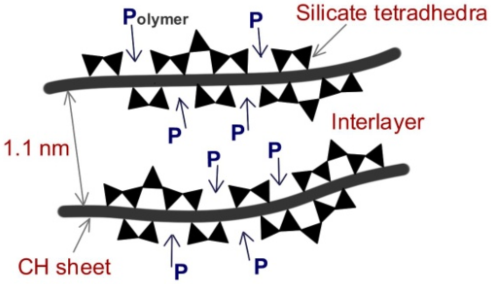

Fig. 2 Schematic of polymer-modified C-S-H nanostructure

4 Concluding Remarks

Significant advancements have been made in the application of nanotechnology in cement science. The molecular structure of cement-based materials can be modified using organic molecules in order to achieve a certain characteristics. The engineering performance of polymer-modified C-S-H nano-strucutures remains to be investigated. Novel approaches are currently taken at NRC to estimate the extent of ingress of foreign molecules into the modified C-S-H. Strength and elasticity of polymer-modified C-S-H materials can also be measured on compacted powder specimens. Producing a new range of construction materials is promising.

References

1. Bartos, P.J.M.: Nanotechnology in construction: A roadmap for development. In: Proceedings of the 2nd International Symposium on Nanotechnology in Construction, Bilbao, Spain, November 13-16, 2005, pp. 27–36 (2005)
2. Dry, C.M., Corsaw, M.J.T.: A time-release technique for corrosion prevention. Cem. Concr. Res. 28(8), 1133–1140 (1998)
3. Dry, C.M.: Alteration of matrix permeability and associated pore and crack structure by timed release of internal chemicals. Ceram. Trans. 16, 729–768 (1991)
4. Reddy, B.R., Crook, R.J., Chatterji, J., King, B.J., Gray, D.W., Fitzgerald, R.M., Pwell, R.J., Todd, B.L.: Controlling the release of chemical additives in well treating fluids, US. Patent 6,209, 646 (2001)

5. Tatematsu, H., Nakamura, T., Koshimuzu, H., Morishita, T., Kotaki, H.: Cement additive for inhibiting concrete deterioration, US. Patent 5,435, 848 (1995)
6. Raki, L., Beaudoin, J.J., Mitchell, L.D.: Layered double hyroxides-like materials: nanocomposites for use in concrete. Cem. Concr. Res. 34, 1717–1724 (2004)
7. Raki, L., Beaudoin, J.J.: Controlled release of chemical admixtures. Canadian Patent # CA 2554347, US patent Application US 2007/0022916 A1 (2007)
8. Kantro, D.L.: Influence of water-reducing admixtures on properties of cement pastes-a miniature slump test. Cem. Concr. and Aggre. 2(2), 95–102 (1980)
9. Taylor, H.F.W.: Cement Chemistry, 2nd edn., p. 459. Thomas Telford, London (1997)
10. Alizadeh, R., Beaudoin, J.J., Ramachandran, V.S., Raki, L.: Applicability of Hedvall effect to study the reactivity of calcium silicate hydrates. Journal of Advances in Cement Research, 1–8 (2009) DOI: 10.1680/adcr.2008.00008
11. Pellenq, R.J.-M., Lequeux, N., Van Damme, H.: Engineering the bonding scheme in C–S–H: The iono-covalent framework. Cem. Conc. Res. 38, 159–174 (2008)
12. Constantinides, G., Ulm, F.-J.: The effect of two types of C-S-H on the elasticity of cement-based materials: Results from nanoindentation and micromechanical modeling. Cem. Conc. Res. 34, 67–80 (2004)
13. Feldman, R.F., Sereda, P.J.: A model for hydrated Portland cement paste as deduced from sorption-length change and mechanical properties. Matériaux et Construction 1, 509–520 (1968)
14. Alizadeh, R., Beaudoin, J.J., Raki, L.: C-S-H (I) - A Nanostructural model for the removal of water from hydrated cement paste. J. Am. Ceram. Soc. 90, 670–672 (2007)
15. Alizadeh, R., Beaudoin, J.J., Raki, L.: Dynamic mechanical response of Calcium-Silicate-Hydrate systems, 47 (2009) (under preparation)
16. Matsuyama, H., Young, J.F.: Intercalation of Polymers in Calcium Silicate Hydrate: A New Synthetic Approach to Biocomposites? Chem. Mat. 11, 16–19 (1999)
17. Beaudoin, J.J., Drame, H., Raki, L., Alizadeh, R.: Formation and properties of C-S-H - HDTMA nano-hybrids. J. Mat. Res. 23, 2804–2815 (2008)
18. Beaudoin, J.J., Patarachao, B., Raki, L., Alizadeh, R.: The interaction of methylene blue dye with calcium-silicate-hydrate. J. Am. Ceram. Soc. 92, 204–208 (2009)
19. Beaudoin, J.J., Drame, H., Raki, L., Alizadeh, R.: Formation and properties of C-S-H - PEG nano-hybrids. Mat. Struct., 1–6 (2009) DOI: 10.1617/s11527-008-9439-x
20. Minet, J., Abramson, S., Bresson, B., Franceschini, A., Van Damme, H., Lequeux, N.: Organic calcium silicate hydrate hybrids: a new approach to cement based nanocomposites. J. Mater. Chem. 16, 1379–1383 (2006)
21. Franceschini, A., Abramson, S., Mancini, V., Bresson, B., Chassenieux, C., Lequeux, N.: New covalent bonded polymer-calcium silicate hydrate composites. J. Mater. Chem. 17, 913–922 (2007)
22. Matsuyama, H., Young, J.F.: Synthesis of calcium silicate hydrate/polymer complexes: Part I. J. Mater. Res. 14, 3379–3388 (1999)