The Effect of SWCNT and Other Nanomaterials on Cement Hydration and Reinforcement

Jon Makar

Abstract. Additions of nanomaterials to cement pastes and concretes may have a significant effect on the performance of ordinary Portland cement (OPC), OPC blends and concrete. Due to the scale of these particles, they may not only modify the bulk behavior of the matrix in a manner similar to micro- and macroscopic additions, but also influence the formation and structure of the C-S-H and other products formed during hydration. Nanoscale additives also have the potential to add new capabilities to concrete. There is therefore growing interest in producing composite materials that include nanomaterials.

Single walled carbon nanotubes (SWCNT) are of particular interest due to their desirable properties as reinforcing materials. They have recently been shown to nucleate the formation of C-S-H during the hydration of ordinary Portland cement (OPC). A series of complementary studies are presented here. The effects of nanotitania, nano-calcium carbonate and nano-alumina dispersed by sonication with OPC on hydration are discussed and compared to the effect of SWCNT dispersed by the same method. The impact of dispersing the SWCNT in blends of admixture and mix water on the hydration of both tricalcium silicate and OPC are investigated. Fracture surfaces of OPC samples blended with all four nano-materials and hydrated for 7 days are analyzed. Classical reinforcing behaviour was identified in the SWCNT/OPC composite alone. A new, nanoscale reinforcing mechanism based on SWCNT bundle pull out is described. The experimental results are used to draw conclusions about the nucleation mechanism in SWCNT composites and on the impact of SWCNT dispersion method on the performance of those composites.

1 Introduction

The addition of nanomaterials, such as nanotubes, nanoparticles and ultrahigh surface area particles to cement and concrete is one of the most promising areas of research for the application of nanotechnology to construction materials. In

Jon Makar
Institute for Research in Construction, National Research Council Canada
1200 Montreal Road, Ottawa, Ontario, Canada
e-mail: jon.makar@nrc-cnrc.gc.ca
addition to being a bulk material formed by chemical reactions [Taylor 1997], calcium silicate hydrate (C-S-H), the main component in hydrated ordinary Portland cement (OPC) and other cements is known to have a fine structure on the order of a few nanometers [Taylor 1997]. As a result, the addition of nanomaterials to hydrating OPC and other cements has the potential to affect both the physical structure of the C-S-H and the hydration reactions themselves.

While studies of nanomaterials mixed with hydrating OPC may provide fundamental insight into the behaviour of cement and concrete, interest in these blends has been driven by the possibility of producing novel and/or superior properties in concrete that may be directly applicable to the construction industry. As a result, considerable attention has been paid both to adding carbon nanotubes and to adding a variety of nanoparticulates to OPC.

Carbon nanotubes (CNTs) are particularly attractive for use in cementitious systems because they appear to be close to ideal reinforcing materials. Ultrahigh aspect ratios [Zheng et al. 2004], extremely high yield strengths [Yu et al. 2000] and moduli of elasticity [Salvetat et al. 1999], and elastic behaviour [Walters et al. 1999] all point to the potential of CNTs in reinforcing applications. In addition, the nanometric diameters of CNT means that if they are well dispersed in a matrix, cracks will encounter one or more reinforcements soon after formation, inhibiting growth at the earliest stage possible. Most work to date has been done on multi-walled carbon nanotubes (MWCNT), which are less expensive and more readily available than single walled carbon nanotubes (SWCNT). There are a number of reports describing both mechanical [Campillo et al. 2004, Ibarra et al. 2006, Li, et al. 2005, Xiang et al. 2005, Cwirzen et al. 2008, Konsta-Gdoutos et al. 2010] and electrical [Li et al. 2007, Wansom et al. 2006] properties of these composites. A recent summary of carbon nanotube/cement composite research [Makar 2009] and an overview of the topic [Raki et al. 2010] can both be found elsewhere.

Less work has been done on OPC/SWCNT composites. SWCNT, however, have higher aspect ratios than MWCNT and individual tube diameters that are close to estimates of the structural spacing of C-S-H layers in hydrated OPC [Taylor 1997b]. They are therefore potentially more desirable as reinforcing materials than are MWCNT. The work presented here is part of a longer term study on the behaviour of cementitious materials when hydrated in the presence of SWCNT.

Early studies [Makar et al. 2005] used Vicker’s microhardness testing to show that the mechanical performance of SWCNT/OPC could be as high as 600% of OPC alone. The improvement in performance was seen to be highest during the first few days of hydration, which suggested that the effect may have been as much due to the SWCNT accelerating the hydration process as due to reinforcing behaviour. A subsequent detailed study [Makar and Chan 2009] that used SWCNT distributed on OPC grains by sonication showed that SWCNT do indeed act to nucleate cement hydration reactions. The work presented here expands on that study. The results of an alternative approach to dispersing SWCNT in cementitious systems using sonication in admixture and mix water are presented. The results of the previous hydration study are also compared to the hydration behaviour of OPC sonicated with 3 different nano-materials (nanoparticulate calcium carbonate and ultra-high surface area alumina and titania). Microscopic evidence for classical