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Review

Reinforced geopolymer composites for enhanced material greenness and durability

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ABSTRACT

The environmental impact of Ordinary Portland Cement (OPC) is significant because its production emits large amounts of CO_2. Further, OPC durability is limited largely due to inherent brittleness. This review examines the environmental and economic impacts of OPC. Using supplementary cementitious materials to enhance material greenness or produce alternative binders such as geopolymers is discussed. This is followed by a review of recent efforts to increase durability through fiber reinforcement. Finally, the current state of the art of geopolymer composites (with both high material greenness and high durability) is discussed along with opportunities and challenges for these promising materials.

Contents

1. Introduction

Since its invention in the early 1800s, concrete made from Ordinary Portland Cement (OPC) has become not just the world's most widely used building material, but the second most widely used material of any kind (behind only water) (Duxson & Provis, 2008). The sustainability of OPC-based infrastructure systems is dictated by two factors: *material greenness* and *durability*. The material greenness of cementitious systems is a product of three factors: virgin resources consumed (water, limestone, etc.), pollutants produced during processing (primarily gaseous CO_2 during the calcination of raw materials), and embodied energy (i.e. energy consumed during production, transportation, and installation of the material). As the virgin resources consumed, wastes produced (especially gases such as CO_2), and energy consumed during processing are decreased on either a volumetric or mass basis, the

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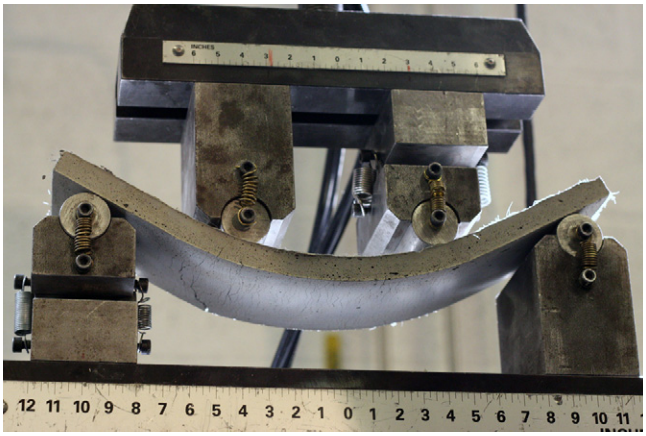

Fig. 1. Fiber reinforcement of cementitious systems can produce distributed microcracking and ultra-ductile behavior, leading to increased durability. (Image courtesy University of Michigan News Media).

material greenness of the system is increased. Durability (correlated to the frequency and intensity of maintenance required over a given structure's service life, and the length of time before the repair or rehabilitation of that structure is necessary) dictates the service life of a structure, and is limited by the physical nature of OPC: compared to other infrastructure materials such as wood or metal, concrete is brittle and cracks under a combination of mechanical and environmental loading, which leads to the deterioration of mechanical properties.

New building materials that enhance *both* material greenness and durability could reduce long-term costs by eliminating the need for the replacement of non-obsolescent structures, and reduce the environmental impact of the built environment. Improvement of both of these two aspects of infrastructure materials will lead to systems with enhanced sustainability.

This paper reviews some of the strategies used to reduce the environmental impact of the worldwide cement industry. First, the use of supplementary cementitious materials (SCMs) either in blended cements or as precursors for alkali-activated geopolymers, an alternative binder system, is examined. Second, increasing durability by suppressing brittleness in favor of ductile behavior through the use of fiber reinforcement is discussed, followed by a brief review of recent attempts to combine these two research paths in fiber reinforced geopolymer composites featuring both enhanced material greenness and high durability (Fig. 1). Though these composite systems face many challenges, they show promise as one of many approaches for increasing the overall sustainability of the built environment.

2. Ordinary portland cement: Environmental impact

Worldwide, 2.8 Gt[1] of OPC was produced in 2009, equal to nearly 6 km^3. Although production in the U.S. has declined from the 2006 high of 99 Mt to about 70 Mt in 2010, production by other major producers (China, 1.4 Gt; India, 180 Mt; Japan, 60 Mt) ensured worldwide production remained at roughly 2008 levels. This level, in turn, is up 78% from 2000 (Gartner, 2004; van Oss, 2010). OPC production is expected to increase both as the world population doubles by the end of the century and as developing nations build modern infrastructure systems (Lawson & Dragusanu, 2008).

In industrialized nations, OPC production will continue to increase so that it can meet the needs of new construction and the deterioration of existing infrastructure. The U.S. alone is estimated to have 7 billion m^3 of concrete[2] currently in place, the majority of which is at least 20 years old, and 350 million m^3 are being added each year (Emmons & Sordyl, 2006). Although a concrete structure can have a lifespan of nearly a century, even under harsh conditions, some systems need costly maintenance after as little as five years (Emmons & Sordyl, 2006).

This use of OPC to create modern infrastructure has come at the cost of significant quantities of CO_2 released to the atmosphere. Chemically, OPC is a mixture of tri- and dicalcium silicate (Ca_3SiO_5 and Ca_2SiO_4, respectively; sometimes written $3CaO{\cdot}SiO_2$ and $2CaO{\cdot}SiO_2$ or as C_3S and C_2S in cement chemist's notation). OPC production relies on the calcination of limestone ($CaCO_3$) and silica (SiO_2) at high temperatures. The production of 1 ton of cement emits roughly ½ ton of CO_2 as a direct result of this chemical reaction (Hardjito, Wallah, Sumajouw, & Rangan, 2004):

$$5CaCO_3 + 2SiO_2 \underset{1450\,^\circ C}{\longrightarrow} Ca_3SiO_5 + Ca_2SiO_4 + 5CO_2$$

When the tri- and dicalcium silicates are hydrated, they create calcium silicate hydrates (C–S–H, in cement chemist's notation) that are the strength-bearing phase of OPC and $Ca(OH)_2$:

$$Ca_3SiO_5 + Ca_2SiO_4 + 10H_2O \rightarrow 2(3CaO{\cdot}2SiO_2{\cdot}3H_2O) + 4Ca(OH)_2 + 173.6\,\text{kJheat}$$

It should be noted that (a) these equations are generalizations that do not take into account minor phases or certain additives, such as gypsum, that are used to fine-tune properties, and (b) the exact ratios of tri- and dicalcium silicates produced in OPC, and thus the exact stoichiometric composition of the C–S–H will vary.

Countries with the largest demand for cement have made substantial progress in switching from inefficient, small-scale kilns to kilns of greater efficiency (most notably China, where modern kilns are planned to produce 95% of Chinese OPC by 2030) (Taylor, Tam, & Gielen, 2006). Since the CO_2 created by calcining limestone is an intrinsic part of the chemical reactions involved in producing OPC, and since highly efficient kilns are already near the theoretical thermodynamic limit, appreciable further reductions in these emissions would require changes in the chemistry of OPC formulations. Altogether, the cement industry contributes a total of 5–8% of worldwide anthropogenic CO_2 emissions (Damtoft, Lukasik, Herfort, Sorrentino, & Gartner, 2008; Davidovits, 1994; Duxson & Provis, 2008; Duxson, Provis, Lukey, & van Deventer, 2007; Hendriks, Worrell, Jager, Blok, & Riemer, 2004; Scrivener & Kirkpatrick, 2008; Worrell, Price, Martin, Hendriks, & Meida, 2001).

Further, the production of OPC is an energy-intensive process. Fuels consumed in cement kilns and used to generate power for grinding equipment are estimated to produce another ½ ton of CO_2 and consume 4–5 GJ of energy for each ton of OPC produced. This amounts to 5% of worldwide industrial energy consumption (Hendriks et al., 2004; Phair, 2006; Scrivener & Kirkpatrick, 2008; Taylor et al., 2006; Worrell et al., 2001). Kilns and grinding equipment are already highly optimized, and it is likely that their designs will remain the most efficient options for decades to come.

It should be noted that the environmental impact of OPC is large mainly because of the sheer volume that is produced every year; compared to other materials, it is relatively green. For instance, the embodied energy (the energy required to produce the material, not including the energy required to transport or install it)

[1] 'Ton' refers to the American short ton (2000 lbs), as opposed to the metric ton (1000 kg or 2200 lbs). Here, American short tons are used exclusively.

[2] Concrete is a mixture of OPC and aggregates. In practice, pure OPC is rarely used; concrete is more common.