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An Analysis upon Various Developments of Cement Based Materials: A Review

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Abstract – Cement-based materials are widely used in the civil infrastructure. Polymers as admixtures can improve the properties, particularly in relation to water absorption reduction, toughness enhancement, vibration damping and increase of the bond strength of cement to reinforcements. Polymeric admixtures include particles, short fibers and organic liquids. Latex in the form of an aqueous particle dispersion is most common. Other than being used as admixtures, polymers are used as partial replacement of fine aggregate, for coating, sealing and repairing concrete and for coating steel reinforcing bars for corrosion protection.

The properties of the designed composites, including the flowability and relative viscosity in fresh state, and the porosity, strength and thermal properties in hardened state are investigated. The porosity of the developed composites is studied by both modeling and experiments. Results indicate that there is a certain amount of closed internal LWA pores in the composites, which contributes positively to a better thermal insulation property. The developed composites have a low thermal conductivity while still retaining sufficient strength. Therefore, the designed composite can be used monolithically as both load-bearing element and thermal insulator.

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INTRODUCTION

Concrete is recognized as the most important man-made construction material in the world. However, Portland cement material which is one of the constituents of the concrete is responsible for about 5-10% of the global CO2 emission (Gibbs, P. et al. ; Meyer 2009). According to the Netherlands Environmental Assessment Agency, in the second half of 2008 half of the annual increase in global CO2 emission is from fossil fuel use and from cement production. The cement industry is aware of the environmental problem of concrete because of the use of Portland cement. In addition, the natural resource of the main raw material limestone, of which cement is made, is being exhausted. The emission of CO2 and the depletion of the raw material make it necessary to find alternatives to reduce the amount of Portland cement needed in the concrete industry. Attempts have been made to partially replace the cement content by pozzolanic or inert fillers.

Cement-based materials (CBM) are the foremost construction materials worldwide. Therefore, there are widely accepted standards for their structural applications. However, for service life designs, current approaches largely depend on CBM strength class and restrictions on CBM constituents.

Consequently, the service life behaviour of CBM structures is still analyzed with insufficiently rigorous approaches that are based on outdated scientific knowledge, particularly regarding the cumulative behaviour since early ages. These results in partial client satisfaction at the completion stage, increased maintenance/repair costs from early ages, and reduced service life of structures, with consequential economic/sustainability impacts.

Despite significant research advances that have been achieved in the last decade in testing and simulation of CBM and thereby predicting their service life performance, there have been no generalized European-funded Actions to assure their incorporation in standards available to designers/contractors.

Cement-based materials are the dominant structural materials for the civil infrastructure. The addition of a minor amount of a polymer to a cement mix can significantly enhance the properties of the resulting material, which is known as a polymer-modified cement-based material. These additives, known as admixtures, can be in the form of polymer particles, short polymer fibers or liquids . Fibers are in general more effective than particles for toughening the cement-based material, but they are more expensive. Any form of polymer is expensive compared to cement. Low cost is critical to the practical viability of a cement-based material.

Immediately after placement, gravitational forces and the local drying environment begin to influence the (micro) structure of a cement paste, mortar, or concrete. Depending on the mixture's water-to-cementitious materials mass ratio (w/c) (and aggregate volume fraction), the initial freshly cast material may be thought of either as a concentrated suspension of rigid particles in water or as a granular water-filled porous media. In the former case, significant settling will be expected to occur, accompanied by bleeding. For present-day Portland cement pastes without admixture additions, for example, measurable bleeding and settling are generally observed for water-to-cement ratios (w/c)N0.4. As the solid particles settle and a corresponding volume of water rises to the top of the specimen, a microstructural (porosity/density) gradient will be established through the thickness of the specimen. In addition to the concentration and particle size distribution (PSD) of the solids, the details of this gradient will depend also on the evaporative water loss from the specimen's top surface, e.g., the drying conditions.

X-ray absorption measurements have been previously applied to examining these microstructural gradients for cement pastes cured under sealed and drying conditions. In the former case, as particles settle, the volume fraction of particles as a function of depth assumes a fairly linear profile (with significant local variations) varying from a higher concentration of particles at the bottom of the specimen to a lower concentration at the top. A lower transmission of the X-ray signal (lower normalized counts, where the counts transmitted have been normalized by the counts transmitted through a reference specimen) indicates a higher concentration of particles, as the cement particles have a much higher X-ray absorption coefficient than water. In this case, the lower concentrations of solids (higher water-filled porosity) established at the top surface during the first few hours of sealed curing may persist throughout the life of the material, resulting in a surface layer that is weaker and that may be much more susceptible to scaling phenomena.

It is an incontrovertible fact that the fineness of Portland cements have increased during the past 50 years and are continuing to increase. This paper summarizes the mean values from three surveys as presented by the Portland Cement Association and also includes individual results from the Cement and Concrete Reference Laboratory (CCRL) proficiency sample program compiled during the past 40 years. While it can be argued that there is no guarantee that the cements selected by CCRL are representative of the cements available from the industry as a whole, taken together. Many cements with a fineness of 400 m^2/kg to 420 m^2/kg are currently available. One of the main reasons for the move towards finer cements has been the ever increasing emphasis on high early-age strengths and fast track construction by much of the industry. Finer cements, with their higher surface area, are more reactive at early ages, producing the desired higher early-age strengths. Since most cement producers are hesitant to produce a wide range of products, the same Type I/II cements that are manufactured for high early-age strength applications (high rise construction, etc.) are also employed in pavements and bridge decks, where long term durability may be much more critical than early-age strength.

Global per capita consumption of concrete has increased since 1970 from less than 1 tonne per person per year to nearly 2.5 tonnes per person per year today. By 2030, it is projected to increase to more than 3 tonnes per person per year. At the same time, the world population has increased from 3.7 billion to more than 7 billion people, meaning that 20 Gt of concrete is placed in service each year. To meet infrastructure needs in regions where population growth is highest, cement production has increased steeply, more than doubling in Africa and in the former Soviet Union and more than tripling in Asia during 2001–2014 alone. 1 In developed regions with more stable or even decreasing populations, infrastructure maintenance, including reconstruction to maintain serviceability and moderate expansion to facilitate economic growth, is apparent through more modest increases of 25–50% in cement production during this period. With worldwide production in excess of 4 billion tonnes annually, Europe is the only region where cement production has remained relatively consistent since the turn of the 21st century. Because of the vast quantity of cement-based materials produced each year, there is much to be gained through improvements in the manufacturing of cement and the production of concrete in terms of meeting societal demand in an increasingly sustainable manner. Even those who are engaged in sustainable development on a global scale and at the forefront of technological innovation recognize the important role key advances in commodity materials such as concrete can play in sustainability. For example, Bill Gates supports the idea—originally proposed by Vaclav Smil's *Making the Modern World: Materials and Dematerialization* —that concrete is the most important human-made material. Gates cites the economic and health (or sanitation-related) benefi ts of concrete construction, while also recognizing that technological advances are needed to reduce the environmental impacts of the material's vast use.

Although "concrete" and "cement" are used interchangeably colloquially, cement is one component of concrete, along with water and fi ne and coarse aggregate (i.e., sand and crushed rock or gravel, respectively). The cement and water combine chemically over time to form heterogeneous hydrated phases that bind the mineral aggregates together, forming a waterresistant composite material. In modern concrete production, a portion of the cement might be replaced or augmented with fi nely divided siliceous or aluminosiliceous minerals (often industrial by-products), called supplementary cementitious materials (SCMs). Chemical admixtures and fi bers might also be included in the mix, and reinforcing bars or strands— commonly carbon steel—can also be used as continuous reinforcement in concrete members.

DURABILITY OF FIBROUS CEMENT BASED MATERIALS

Cement bonded wood has been investigated for more the one hundred years, whereas the industrial utilization of cement bonded particleboard started in the 1930´s. However, most of the innovations have been done in the last 40 years. In the beginning cement bonded composites, particularly low-density boards, were mainly used for insulating purposes. In 1973, a Swiss company called Durisol was among the first manufacturers that produced a building panel consisting of small wood particles bonded in a cement matrix. Wood-cement board, fibre-cement boards, gypsum fibreboards, and gypsum particleboards are now manufactured in various parts of the world. The opportunity for this industry to expand is substantial, because the raw material is available locally in many nations and, worldwide, the need for durable building products is strong . Fiber cement composite products can be made use of in exterior and interior of a building such as siding, roofing, external cladding, internal lining, floors, walls, building boards, bricks, bracing, fencing and decorative elements. Fiber cement is also used in construction works such as dam, bridge deck, road building, sidewalk, flagstone paving, and so on.

One of the main ingredients of fiber cement products is cellulose fibre from wood or non-wood sources, which are added to reinforce the cement composite. Also, small amounts of chemical additives are utilized to help the process, or provide products with particular characteristics. Depending on their application, fibre-cement materials can offer a variety of advantages over traditional construction materials:

- As compared to wood, fibre-cement products offer improved dimensional stability, moisture resistance, decay resistance, and fire resistance;
- As compared to masonry, fibre-cement products enable faster, lower cost, lightweight construction;
- As compared to cement-based materials without fibres, fibre-cement products may offer improved toughness, ductility, and flexural capacity, as well as crack resistance and “nailability”.

Fibre-cement composite products for residential housing have been generally limited to exterior applications, such as siding, and roofing. Their exterior use has been limited in the industry due to degradation to ambient wetting and drying. Thus, these components must be currently maintained by painting to avoid moisture problems. Furthermore, the applications of these composite products are non-structural (i.e., non-load-bearing) in nature. Durability, toughness, high dimensional stability, resistance against environmental influences such as biodergradation of weatering but also availability of the raw material as well as economic factors are features which can make fibre-cement composites superior to conventionally bonded composites . Their primary disadvantages is their vulnerability to decomposition in the alkaline environment present in Portland cement.

Changes in the fibre and fibre/cement interfacial region due to environmental interactions can affect the long-term performance of cement-based composites reinforced with natural fibres. Scanning electron microscopy by Mohr et al. revealed ductile fibre behaviour, i.e., fibre pull-out and Poisson’s effect at fibre tips, for those composite samples subjected to a low number of wet/dry cycles, even though the composites exhibited significant mechanical property losses.

However, the mechanism for this early increased fibre-cement bonding is unknown. One possible explanation for this behavior is the formation of calcium hydroxide or ettringite acting to density the transition zone around the fibres. Calcium hydroxide is soluble product of cement hydration that may reprecipitate in voids (i.e., fibre-cement interface) during wet/dry cycling. Ettringite may also form through a similar process known as delayed ettringite formation .

Analyzing cement bonded particleboards by means of X-ray diffractometry, diffusion of cement molecules, especially calcium, magnesium and silicon, into the cell wall of wood particles was observed. The alkaline environment arises during cement hydratation, where calcium hydroxide is produced; the result is an alkaline (pH = 12.5) cement paste. Since hemicelluloses are noncrystaline and alkalinesoluble, they dissolve in the cement paste and affect cement crystallization. Additionally, the acid and alkaline components, which penetrate into the wood, will damage the wooden structure, which results in extra loss of strength. Furthermore the degradation products, which are developed by the penetration of acid and alkaline components, will influence hydratation of cement.

POLYMERS FOR CEMENT-BASED STRUCTURAL MATERIALS

Cement-based materials are the dominant structural materials for the civil infrastructure. The addition of a minor amount of a polymer to a cement mix can significantly enhance the properties of the resulting material, which is known as a polymer-modified cement-based material. These additives, known as admixtures, can be in the form of polymer particles, short polymer fibers or liquids . Fibers are in general more effective than particles for toughening the cement-based material, but they are more expensive. Any form of polymer is expensive compared to cement. Low cost is critical to the practical viability of a cement-based material.

Polymer particles as admixtures - Polymer particles used as admixtures can be in the form of a dry powder or an aqueous dispersion of particles. The latter form is more common. Either form as an admixture results in improved joining of the mix constituents (e.g., sand), due to the presence of interweaving polymer films. The improved joining leads to superior mechanical and durability characteristics.

Aqueous dispersions of polymer particles are more effective than dry polymer powder for the development and uniform distribution of polymer films . The most common form of polymer in aqueous dispersions is latex, particularly butadiene-styrene copolymer. The dispersions are stabilized by the use of surfactants. In polymer-modified cement-based material, polymer particles are partitioned between the inside of hydrates and the surface of anhydrous cement grains.

The presence of the polymer results in improved pore structure thereby decreased porosity. Furthermore, the workability is enhanced and the water absorption is decreased. The enhanced workability allows the use of lower values of the water/cement ratio. The rate of hydration is reduced by the presence of the polymer.

The addition of a polymer tends to increase the flexural strength and toughness, but lower the compressive strength, modulus of elasticity and hardness. Furthermore, the polymer addition is effective for enhancing the vibration damping capacity, the frost resistance, and the resistance to biogenic sulfuric acid corrosion (relevant to sewer systems). In addition, polymer addition imparts stability and thixotropy to grouts and enables control of the rheology and stabilization of the cement slurry against segregation.

Dry polymer particles used as an admixture can be water-redispersible polymer particles, such as those obtained by spray drying aqueous dispersions. Examples are acrylic and poly (ethylene-vinyl acetate) .

Redispersibility may be attained by the use of functional monomers. The effectiveness of redispersible polymer particles depends on the cement used. A special category of polymer particles is superabsorbent particles (hydrogel), which serve to provide controlled formation of water-filled macropore inclusions (i.e., water entrainment) in the fresh concrete .

The consequence is control of self-dessication. Another kind of superabsorbent polymer can hardly absorb alkaline water in fresh/hardened concrete, but can absorb much neutral/acidwater and make gel. Thus, when neutral water is poured on concrete after setting, the concrete is coated with the gel and thus can be kept without drying.

Organic liquids as admixtures - Organic liquid admixtures can be polymer solutions (involving water-soluble polymers such as methylcellulose, polyvinyl alcohol and polyacrylamide) or resins (such as epoxy and unsaturated polyester resin). The liquid form is attractive in its ease of uniform spatial distribution, and hence effectiveness in even a small proportion. In contrast to polymer solutions, particles (including particle dispersions) tend to require a higher proportion in order to be comparably effective.

Polymer solutions as admixtures can serve to optimize the air void distribution and rheology of the wet mix, thereby improving workability with low air content. They are important for macrodefect-free (MDF) cements, which are attractive in their high flexural strength. However, MDF cements have poor water resistance, due to the water soluble polymers in them.

Short polymer fibers as admixtures- Short fibers rather than continuous ones are used because they can be incorporated in the cement mix, thereby facilitating processing in the field. Furthermore, short fibers are less expensive than continuous ones. Polypropylene, polyethylene and acrylic fibers are particularly common, due to the requirements of low cost and resistance to the alkaline environment in cement-based materials.

Compared to carbon, glass and steel fibers, polymer fibers are attractive in their high ductility, which results in high flexural toughness in the cement-based material. Combined use of short polymer fiber and polymer particle dispersion (e.g., latex) results in superior strength (tensile, compressive and flexural) and flexural toughness compared to the use of fiber without polymer particle dispersion.

SUPPLEMENTARY CEMENTITIOUS MATERIALS AND ALTERNATIVES

Historically, blends of portland cement and fi nely divided, largely amorphous silicates and aluminosilicates (“pozzolans,” a type of SCM) have produced high-quality concrete; this practice contributes to sustainability not only by reducing the cement clinker fraction (and proportionate embodied energy and GHGs) but also by potentially improving durability through increases in impermeability and decreases in leachable and reactive phases, such as hydrated lime. Materials scientists today employ techniques such as thermal analysis, synchrotron and x-ray microdiffraction, tomography, electron microscopy, and nuclear magnetic resonance spectroscopy to characterize fundamental reactions between ancient pozzolanic volcanic ash, natural zeolites, and lime, as well as their interactions with their environment. Such fundamental studies provide new insights into the persistence of these ancient cementitious materials over millennia and also form the foundation for the modern production of low-energy binder systems, based on naturally occurring and industrialby-product siliceous and aluminosiliceous sources in combination with portland cement or other calcium-rich and alkaline materials.

Today, combining cement with pozzolans or SCMs, relatively inexpensively sourced as industrial by-products such as fl y ash from coal-burning power plants and slag from blast-furnace steel production, is common practice. India and China consume 65% of the cement produced worldwide each year, and both rely heavily on coal as a power source.

ELECTRICALLY CONDUCTIVE CEMENT-BASED MATERIALS

Cement-based materials have received much attention in relation to their mechanical properties, due to their importance as structural materials. However, the need for a structural material to be able to serve one or more non-structural functions while retaining good structural properties is increasingly recognised[1]. This is because the use of a multifunctional structural material in place of a combination of a structural material and a non-structural functional material (e.g., a structural materia] with an embedded non-structural functional material) reduces cost, enhances durability and repairability. increases the functional volume, avoids degradation of the mechanical properties, and simplifies design. Non-structural functions include sensing, actuation. heating, corrosion protection, self-healing, thermal insulation, heat retention and electromagnetic interference (EMI) shielding."

Electrically conductive cement-based materials are one category of multifunctional cement-based materials.' [1] The conductivity is attractive for electrical grounding, lightning protection, resistance heating (e.g., in de-icing and building heating), static charge dissipation, electromagnetic interference shielding, thermoelectric energy generation and for overlays (electrical contacts| used in the cathodic protection of steel reinforcing bars (rebars) in concrete.

Electrical conduction - The cement matrix is electrically attractive due to its electrical conductivity, which is in contrast to the non-conductive behaviour of most polymers. Due to the conductivity of the cement matrix, an electrically conductive admixture (i.e.. a conductive filler) in a cement-matrix composite can enhance the conductivity of the composite even when the volume fraction of the admixture is below the percolation threshold, which refers to the volume fraction above which the admixture units touch to form a continuous conduction path. The percolation threshold is determined from the variation of the electrical resistivity with the volume fraction of the conductive admixture. The electrical resistivity abruptly decreases by orders of magnitude at the percolation threshold.' In most cases, the percolation threshold decreases with increasing aspect ratio and with decreasing unit size of the admixture.

Applications - Electrical grounding is needed for buildings and other structures which involve electrical power. Lightning protection is needed for tall buildings. Metals such as steel are commonly used for these applications. However, the use of electrically conductive concrete to diminish the volume of metal required is attractive for cost reduction, durability improvement and installation simplification.

Static charge dissipation is needed for structures that come into contact with sensitive electronic devices. Metals and conductor filled polyiner-matrix composites are used for this purpose. However, the use of electrically conductive concrete for this application allows large volumes of structure to have the ability for static charge dissipation.

Due to the environmental problem associated with the use of fossil fuels and due to the high cost of solar heating, electrical healing is increasingly important. Although electric heat pumps are widely used for the electrical healing of buildings, resistance heating is a complementary method which is receiving increasing attention due to the low costs for its implementation and control, its adaptability to localised healing (e.g., the heating of a particular room of a building), ils nearly 100% efficiency of conversion of cicctrical energy to heat energy, and the increasing demand of safety and the quality of life. Resistance heating is needed in buildings and for the de-icing of driveways, bridges, highways and airport runways. De-icing is valuable for hazard mitigation. The alternative technique or' snow removal (shovelling) is labour intensive and takes time, in contrast to the automatic and continuous nature of de-icing by resistance heating.

MECHANICAL PROPERTIES OF A CEMENT-BASED MATERIAL CONTAINING CARBON NANOTUBE

Carbon nanotube (CNT) is a novel and nano-sized fiber with outstanding mechanical and physical properties. Theoretically, Young's modulus, tensile strength and fracture strain of an individual CNT fiber can reach 1 TPa, 100 GPa and 15%, respectively. Also, CNT has a high specific surface area with a value of up to 1000 $m^2.g^{-1}$. Due to these excellent mechanical and physical properties, CNT has been added to traditional materials, such as cement-based materials and polymers, for enhancement of their properties.

During the service life of concrete structures, durability is an important issue that must be considered. A number of severe environmental factors can deteriorate the mechanical performances of structural materials. For example, the hot dry environment is often considered to damage the durability of cement-based materials due to insufficient hydration, as well as the freeze-thaw cycling (FT) which can induce a series of internal micro-cracks in cement-based materials. In continental areas such as central Asia and parts of North America concrete could even experience both of these two extreme conditions (i.e., cold weather in winter and hot climate in summer), and therefore designers need information about the performances of the materials when wet and frozen in winter as well as when hot and dry in summer . Drying shrinkage and insufficient hydration are of great concern for concretes in hot and dry climates. Besides, additional stress is generated in concretes by the FT effect and the materials become easy to crack and get surface scaling, which may speed up the ingress of detrimental ions and the degradation of mechanical properties. In these areas, cement-based materials are required to have satisfactory performance in such severe environments.

Based on research, the mechanism for using CNT as a reinforcing component in cement-based material is based on its bonding, bridging and mesh filling effects, which redistribute the inner stress and inhibit the propagation of micro-cracks. The influences of CNT on the properties of cement-based materials from the aspect of durability can be divided into two series. On the one hand, some researchers have found that CNT is helpful for improvement of durability. Makar et al. dispersed single-walled CNT (SWCNT) by sonication and observed from the cracks in SEM micrographs that SWCNT acted as bridges and reinforced the matrix; Han et al. found that multi-walled CNT (MWCNT) could decrease the absorption coefficient, water permeability and gas permeability of cement-based materials. On the other hand, CNT was also reported to have detrimental effects on durability. Del et al. detected a slight increase in porosity when CNT was added to cement-based material; the results also showed that the addition of CNT increased the degradation of concrete under carbonation and promoted the ingress of chloride ions; the reason for the higher corrosion level is that higher CNT dosage leads to higher conductivity and therefore a higher galvanic coupling effect from the CNT to the steel reinforcement. In summary, the reasons for getting the two contrary results from different works are complicated, but may include the different dispersion methods and dosages of CNT used in the studies.

During the use of CNT in cement-based materials, dispersion of CNT is an important step and influences the properties obtained. At the moment, dispersions of CNT into water by means of surfactant and sonication are commonly used. Konsta-Gdoutos et al. found that surfactant in combination with sonication could effectively disperse CNT in water. During the sonication, bubbles created by waves release high levels of energy and separate individual CNT from bundles. Besides, surfactant can be absorbed to the CNT surface and protects CNT from agglomeration. However, the surfactant applied was also found to act as an air entraining agent and resulted in adverse effects to the mechanical properties , while longer sonication pretreatment on the CNT may break its structure . In 2013, Saravanan et al. used a high energy ball milling process to disperse CNT into AA 4032 nanocrystalline matrix and found no structural damage in the CNT. Therefore, in this study, the ball milling dispersion method was used to disperse CNT during the casting of the samples.

CONCLUSIONS

This article addresses the development of cement-based lightweight aggregates composites aiming at a good balance between a low thermal conductivity and good mechanical properties. The designed lightweight composites can be applied monolithically as concrete structure, as both structural load-bearing elements and thermal insulator.

A comparative review of the effectiveness of various electrically conductive admixtures (steel fibres, steel dust, carbon fibres, carbon nano fibre, coke powder and graphite powder) for ccment-bascd materials has shown that steel fibre of diameter 8 um is most effective for lowering the electrical resistivity and providing EMI shielding. Carbon fibre (15 /<m diameter) is more effective than carbon nanofihre (01 um diameter), coke powder or graphite powder for lowering the resistivity.

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